PRINCIPLES OF CHEMICAL ENGINEERING

WALKER LEWIS AND MCADAMS

Chemical Engineering Series

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PRINCIPLES OF CHEMICAL ENGINEERING

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CHEMICAL ENGINEERING SERIES

PRINCIPLES OF CHEMICAL ENGINEERING

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SECOND EDITION

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PREFACE TO THE SECOND EDITION

In the preparation of this new edition every effort has been made to correct any errors or lack of clarity in the old text and to bring the book up to date in all fields in which recent progress has made this desirable. In a number of places this has required expansion. In the chapter on Flow of Heat, the constants and the form of several equations have been modified slightly to make them more generally applicable and conform more closely with recently determined data. The quantitative treatment of gas producers has been amplified. In the discussion of rectification, graphical methods of computation have been substituted for the algebraic technique employed in the first edition, because the former are more rapid and the significance of the steps much more readily visualized. At the request of a large number of users of the book, there has been added as an Appendix a list of problems for solution.

It was originally intended to incorporate in the first edition chapters covering those processes of diffusion which include the operations of gas scrubbing, percolation filtration, lixiviation, and the like, but it was impossible to do so without unduly delaying publication. This whole subject was then in a decided state of flux, its theoretical foundations were imperfectly developed and the technique of the exact solution of practical problems almost unknown. Since then the subject has crystallized rapidly and two chapters covering these topics have been added. The first deals with the specific application of the underlying principles of diffusion, which govern all interaction between phases and which have already been discussed and applied in the chapters on Drying and Distillation, to those types of problems particularly characteristic of the operations here treated. Special emphasis is laid upon the questions of equilibrium and reaction rate, for constant conditions of operation at any specific point. The second chapter is devoted to a description and discussion of standard operating methods and equipment and to the technique of the quantitative application of the underlying

principles developed in the preceding chapter to the solution of typical problems. Throughout the treatment emphasis is laid upon the analogies which exist even in cases superficially divergent in character.

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CAMBIDGE, MASS.
July, 1927.

PREFACE TO THE FIRST EDITION

JUST as the arts of tanning and dyeing were practiced long before the scientific principles upon which they depend were known, so also the practice of Chemical Engineering preceded any analysis or exposition of the principles upon which such practice is based. The unit operations of chemical engineering have in some instances been developed to such an extent in individual industries that the operation is looked upon as a special one adapted to these conditions alone, and is, therefore, not frequently used by other industries. All important unit operations have much in common, and if the underlying principles upon which the rational design and operation of basic types of engineering equipment depend are understood, their successful adaptation to manufacturing processes becomes a matter of good management rather than of good fortune.

In this book we have attempted to recall to the reader's mind those principles of science upon which chemical engineering operations are based, and then to develop methods for applying these principles to the solution of such problems as present themselves in chemical engineering practice. We have selected for treatment basic operations common to all chemical industries, rather than details of specific processes, and so far as is now possible, the treatment is mathematically quantitative as well as qualitatively descriptive. We venture to hope that the book will stimulate engineers to *design* apparatus adapted for any particular purpose, rather than just to *build* it and then to rely on large scale experimentation with expensive changes in construction to effect efficient operation.

This book may be divided roughly into five parts.

First, the principles of stoichiometry are reviewed, special emphasis being laid upon the utility of the pound mol as a unit for calculation, and the relative ease with which the units of one

system may be transformed into those of another system. Experience has taught us that practicing engineers as well as students fail to realize the vast amount of useful data there is available, largely in chemical literature, and hence in the metric system. There is a lack, also, of an effort to select properly those data to be recorded in laboratory experimentation and factory operation, in order that any definite information may be obtained. Frequently also data are used inadequately, and much desired information overlooked because of faulty interpretation. Therefore we have introduced illustrative problems and their solution throughout the book, in which we believe the reader may find helpful suggestions relative to the plan of an experimental run, the data to choose, and the method of solution and interpretation to adopt. These problems should not be looked upon as nuts for students to crack, but as an integral part of the text vitally illustrative of the subject matter considered.

Second, because of their fundamental importance the phenomena accompanying the flow of heat and the flow of fluids, together with the laws governing these operations are considered in detail. An interchange of heat is a necessary step in almost every chemical reaction and must be provided for adequately to insure continuous operation. So far as possible we have illustrated the use of the more complex equations with problems stated and solved.

Third, fuels and their efficient combustion are treated at considerable length in order to render clear the important relationships here involved. More economical use of fuel will be demanded in the future.

Fourth, processes of crushing and grinding, mechanical methods for separating materials, together with filtration in its many different forms, are given a descriptive treatment with a mathematical analysis when such seems advantageous.

Fifth, those processes depending upon vaporization are treated from the common standpoint of vapor pressure equilibria. With drying in its many phases we consider also humidification, dehumidification and water cooling. Evaporation and distillation are placed in separate chapters.

The greater part of the text has for some time been in use as students' notes at the Massachusetts Institute of Technology, and at times has been drawn upon freely by both staff and students in their published papers.

It may seem to the reader that brevity is sometimes sacrificed by repetition of ideas, and that the detailed derivation of mathematical equations is unnecessarily separated from the descriptive matter to which they relate. Experience in teaching this subject has proven the desirability of this method of treatment.

This book is the outgrowth of extensive engineering practice in the course of which we have profited by many ideas offered in the way of suggestions, criticism or advice. We have assayed these ideas in the crucible of experience, and have endeavored to incorporate those found to be of value. These contributions have come from so many sources that detailed acknowledgment here is impossible, but for this very real help we are deeply grateful to our many friends.

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PRINCIPLES OF CHEMICAL ENGINEERING

CHAPTER I

ELEMENTS OF INDUSTRIAL STOICHIOMETRY

Introduction.—Science makes it possible to predict the future through the ability to reason from known facts and conditions, or to make a mathematical calculation based upon established data, and thus to reach a rational conclusion in advance of the actual realization of the phenomenon. However, the ability to state mathematically the relationship between any two or more factors frequently calls for a knowledge of method of analysis not possessed by the average college student or young man in the works. The English speaking chemical engineer is accustomed to find his scientific data given in metric units and to carry on his laboratory calculations in grams, centimeters and liters. Since the calculations arising in the quantitative application of scientific data and methods in the field of applied chemistry are often in themselves very complicated and involved, it frequently requires only the confusion occasioned by the necessity for converting conceptions and data formulated heretofore in the metric system, into corresponding English terms, to deter the technical man from making the attempt.

It is the purpose of this chapter to recall to the reader the principles upon which such estimations are based, and to point out certain methods of calculation by which experimental data may be more readily interpreted in terms of factory conditions, and made available for the solution of everyday problems, and the confusion occasioned by handling data in two systems minimized or eliminated.

LAWS USED IN INDUSTRIAL STOICHIOMETRY

Chemical Engineering calculations involve three simple basic generalizations of universal usefulness. These are the Law of the Conservation of Elements, the Law of the Conservation of Energy, and the Stoichiometric Relationships[1] as to combining weights expressed in chemical formulas and equations. The importance of these three laws arises from the fact that they are quantitatively applicable under all conditions, and at least the first and third of them are used, sometimes implicitly, in the course of every chemical calculation. Faraday's Law of Electrolysis is also quantitatively applicable under all conditions, but is employed only in the solution of a special type of problem.

Other laws or principles such as the Law of Mass Action, of Reaction Rate, of the Vapor Pressure Relations of Solutions, and similar generalizations of Physical Chemistry, are of only limited applicability, in the present state of our knowledge, owing to the wide deviations from and nonconformity to these laws in some cases, and must be employed quantitatively with intelligent caution. Similarly such principles as the Second Law of Thermodynamics, the generalizations regarding the equilibria and the energy requirements of chemical reactions that follow from it, and the like, are again not so frequently used, owing in large measure, no doubt, to the complexity of the calculations involved.

USE OF ENGLISH UNITS

Whatever the advantages of the Metric System of units, most readers of this book will be compelled to employ English units in much of their work. Such units will therefore be freely used, and it is hoped to show that the disadvantages of carrying out calculations in the English system and the difficulties of conversion of calculations from one system to the other are greatly overestimated.

THE MOLAL UNIT AND ITS UTILITY

Chemical reactions occur between atoms, either alone or when combined into molecules, and these quantities furnish very convenient units with which to calculate the results of such reactions. Thus the equation

$$\underset{12}{C}+\underset{32}{O_2}=\underset{44}{CO_2}$$

states that one atom of carbon unites with one molecule of oxygen and produces one molecule of carbon dioxide. It also states that 12 parts by weight, be they grams, ounces or tons, of carbon, combine with 32 parts by weight of the same unit of oxygen to furnish 44 parts by weight of CO_2. It is a convenience, therefore, to combine these two ideas and speak of a *gram atom* of carbon or a *pound atom* of carbon, meaning the quantity of carbon in any convenient unit of weight which is represented by the symbol C, and to realize that it will combine with a gram molecule, or a pound molecule or any unit selected, of oxygen. One can then speak of a gram molecule or a pound molecule of any material and mean thereby the number of grams or pounds which is represented by the relative weight of the reacting unit, be it atom or molecule.

But gases are generally measured by volume and analyses are given in volume per cent, while solids are usually measured by weight and analyses expressed in per cent by weight. In practice, therefore, the above equation involves materials usually reported in two different ways. It is a convenience, then, to be able to use a common basis. This is found in the pound molecule, or as contracted, the *pound mol.*

If in 100 cu. ft. of a gas there are 20 cu. ft. of O_2 and 80 cu. ft. of N_2, it contains 20 per cent O_2 and 80 per cent N_2 by volume. According to the accepted hypothesis of Avogadro, equal volumes of all gases contain the same number of molecules. Hence this gas contains 20 per cent O_2 and 80 per cent N_2 on the basis of the *number of molecules present;* that is, of every 100 molecules in the gas, 20 of them are O_2 and 80 are N_2. Furthermore, Avogadro's hypothesis implies that the pressure exerted by any gas at a given temperature is proportional to the number of molecules of that gas per unit volume, while Dalton's law states that, in mixtures of gases, the pressure of each individual component is independent of the presence of the others and the partial pressures of the components are additive, the total pressures being the sum of all the partial pressures. Consequently, for mixtures of gases obeying these two gas laws, the pressure of each component, expressed as a percentage of the total pressure, is numerically equal to the

[1] For a statement of these relationships the reader is referred to any of the standard works on inorganic chemistry.

mol per cent of that component in the mixture and also to its volume per cent.

Consider, for example, the combustion with air of a coke containing 82 per cent carbon, 1 per cent hydrogen, 4 per cent moisture, and 13 per cent ash by weight. For every 100 lbs. of coke there are 6.83 pound atoms of carbon, 0.496 pound mols of hydrogen and 0.222 pound mols of moisture. The ash need not be considered, other than affecting the purity of the coke, as it does not enter into the calculations. Since for gases volume per cent is the equivalent of mol per cent, all quantities are now on a similar basis and the calculations, as will be shown later, are greatly simplified.

Since equal volumes of all gases contain the same number of molecules, it is evident that a certain volume may be chosen, such that under standard conditions of temperature and pressure (0° C. and 760 mm.), it will contain just the number of molecules necessary to weigh the number of pounds or grams expressed by its molecular weight. This volume is found experimentally to be 22.4 liters for the gram mol, equivalent to 359 cu. ft. for the pound mol, and is called the *molal volume*. Unless otherwise noted, throughout this book the *pound* mol and *pound* atom are used, which may be abbreviated to mol and atom, respectively.

The molecular weight of a gas is well defined as the weight in pounds of 359 cu. ft. of the gas, measured under standard conditions (S. C.)[1] of temperature and pressure. In this sense the molecular weight (M. W.) of a mixture of gases can be spoken of as well as that of a single gas. Thus air which is moisture-free has the following average analysis:

Oxygen	20.92 per cent by volume
Nitrogen	78.14
Carbon Dioxide	0.04
Argon, etc	0.90

The average molecular weight of air or any other gas mixture may be calculated by adding together the weights of each component in one molal volume of the mixture as follows:

[1] Throughout the book the abbreviation "S. C." is used to designate "standard conditions."

Component	Mols in 1 mol air	Molecular Weight	Pounds in 1 molal volume air
O_2	0.2092	32.00	6.69
N_2	0.7814	28.02	21.90
CO_2	0.0004	44.0	.02
A	0.0090	40	.36
Total weight of 1 mol of air is			28.97 lbs.,

which for all practical purposes is 29.0.

In most chemical processes the nitrogen is inert, and is analytically determined by difference, the argon and the traces of other noble gases are included with it, and the composition of dry air is frequently taken, for the purpose of such calculations as 20.9 per cent O_2, and 79.1 per cent N_2. The only variable which must be determined experimentally in each case is the moisture content.

Gas Laws.—Since gases are seldom if ever measured at standard conditions, it becomes necessary to know how to find the molal volume at different temperatures and pressures. This can of course be done by the use of the gas equation in the form, $pv=nRT$, where n is the number of gram mols of the gas in question, while R is a single constant applicable to all perfect gases, the numerical value of which depends only on the particular units of pressure, volume, and temperature, (p, v, T) employed.

Obviously similar relationships must obtain in English units. For all gases this gas equation may be written $pv=1544nT$, the quantities being given in English Engineering units, where p is the total absolute pressure in pounds per square foot, v is the total volume in cubic feet, T is in degrees Rankine,[1] while n is the number of pound mols of the gas involved in the calculation.

Instead of substituting the proper values in this equation and solving for the volume, it is often simpler, as will appear in later calculations, to find the volume by multiplying the volume of the gas at standard conditions by a ratio. The gas equation has the advantage whenever work quantities are to be calculated, but the constant in the equation is dependent on the units employed, and as the units are liable to be of different systems, its use would

[1] Equals °F. absolute, *i.e.*, °F.+460.

entail memorizing a number of constants, necessitate a table for the same, or require a more or less laborious conversion of units each time they are given in a different form. Therefore, manipulation of the standard molal volume is the easier operation.

If one writes the equation for the gas under any conditions of temperature and pressure as

$$pv = 1544nT,$$

and under standard conditions as

$$p_0v_0 = 1544nT_0,$$

dividing the first equation by the second and solving for v gives

$$v = v_0 \times \frac{p_0}{p} \times \frac{T}{T_0}.$$

Since in the correction factors applied to v_0 in order to get v, p_0/p and T/T_0 are ratios, and therefore contain no units, they may be expressed in any absolute units of temperature or pressure, so long as the units are the same in any one ratio.

Instead of memorizing this equation it is well to remember only that the volume measured must be multiplied by an absolute temperature ratio and an absolute pressure ratio, and to rely on common sense to determine whether these ratios should be greater or less than unity, according to whether the gas is passing from a lower to a higher temperature or a greater to a smaller pressure, or vice versa.

This relationship will be made clearer by the following examples:

The volume of $\frac{1}{2}$ mol of any gas at 60° F. and 780 mm. pressure is determined by the equation:

Mols of gas	Cu. ft. at S.C.	At 60° F., 760 mm.	
359	520	760	= 185 cu.ft.
2	492	780	

The volume of 25 lbs. of a natural gas containing 85 per cent CH_4 and 15 per cent C_2H_6 at 20° C. and 1 lb. gauge pressure is found as follows:

First, determine the apparent or average molecular weight of the gas.

Since the volume percentage composition based upon 100 units is at the same time the molal percentage relationship,

$0.85 \times 16.07 = 13.65$ lbs. of methane
$0.15 \times 30.11 = 4.52$ lbs. of ethane

18.17 lbs. of mixture

Thus 18.17 is the average molecular weight of this gas mixture. One lb. gauge pressure is equivalent to 15.7 lbs. absolute pressure since one standard atmosphere equals 14.7 lbs. per sq. in. Then the volume is

Mols of gas	Cu. ft. at S.C.	At 20° C.		
25	359	293	14.7	= 497 cu.ft.
18.17		273	15.7	

How many pounds of carbon dioxide are in 1000 cu. ft. of dry flue gas containing 15 per cent CO_2 at 500° F., the barometer being 29.2 in. of mercury? (Normal barometer in inches of mercury is 29.92 or 29.9 for most calculations.)

Cu. ft. at 500° F., 29.2 in.	At 32° F., 29.2 in.	At S.C.	Mols total gas	Mols CO_2		
1000	192	29.2	1	0.15	44	= 9.2 lbs.
	960	29.9	359			

The gas laws in this form are subject only to those limitations with which all are familiar. They cannot be applied without proper modification to gases, the molecules of which associate or dissociate, nor to any gases at high pressures, especially if near their points of saturation. However, the errors involved in applying these laws to the so-called permanent gases up to 15 or 20 atmospheres or even to saturated vapors up to one or perhaps two atmospheres are negligible for most engineering purposes (not over 2 or 3 per cent). Consequently none of the many

refinements of the perfect gas equation are necessary in most industrial calculations.

Heat Units.—In the Metric System heat quantities are measured in gram calories, and in the English in B.t.u. (British thermal units). Because even in English plants the centigrade scale is so extensively used, Davis[1] has recommended the use of the centigrade heat unit[2] (C.h.u.) the heat required to raise one pound of water one degree centigrade, which as will presently appear has certain advantages in thermal calculations. One C.h.u. is obviously 1.8 B.t.u. or 454 gm. cal. The basic quantities in determining the energy effects in chemical systems are the heats of reaction. In the chemical literature heats of reaction are almost always reported as gm. cal. per gm. mol (or kg. cal. per gm. mol). Thus the statement that the heat of combustion of C to CO_2 is accompanied by a positive heat of reaction of 97,000 cal., means that the combustion of one gm. atom of carbon (12 gms.) to form one gm. mol of CO_2 (44 gms.) liberates enough heat to raise 97,000 grams of water 1° C. Obviously then if one lb. atom of carbon (12 lbs.) were burnt, forming one lb. mol of CO_2 (44 lbs.) the heat evolved would suffice to heat 97,000 lbs. of water 1° C., *i.e.*, would develop 97,000 C.h.u. In other words, heats of reaction in gm. cal. per gm. mol are numerically identical with heats of reaction in C.h.u. per lb. mol. This means that if a chemical calculation be carried through, expressing the quantities of the reacting substances in gm. mols or gm. atoms and the heat effects in gm. cal., the same numerical figures apply unchanged to the reaction if the quantities taken were lb. mols or atoms, and the heat effects were C.h.u. By the use of this method, the basic data as to heats of reaction can be taken from metric tables and used directly and conveniently in calculations in English units.

If it be preferred to know the heats of reaction in B.t.u., these quantities expressed in gm. cal. per gm. mol or atom are converted to B.t.u. per lb. mol or atom by multiplying by 1.8.

The gas constant, R, in the gas equation $pv=nRT$, is an energy term, which it is frequently convenient to express in heat units, as for example in estimating the heat equivalent of the external work corresponding to the evolution of any gas against the pressure of the atmosphere. If n be expressed in either gram mols or lb. mols, the value of R in heat units is always 1.985 (approximately 2), the same numerical figure, in both Metric and English units, though the heat quantity obtained by multiplying by nT is in gm. cal. in the Metric system, while in the English system it is in B.t.u. if the Fahrenheit temperature scale be used or in C.h.u. if the Centigrade be employed.

[1] Davis, "Handbook of Chemical Engineering."

[2] Also called the pound-calorie (lb. cal.), Richards, "Metallurgical Calculations," or the "pound-centigrade unit" (P. c. u.).

Molal Heat Capacities, *Gases.*—A further advantage of the use of the mol as unit in calculations lies in the fact that many of the physical properties of substances have relatively simple molal relationships. Thus while the *specific heats* at constant pressure, Cp, of the permanent diatomic gases vary widely (from about 0.2 to over 3.0) their *molal heat capacities, i.e.*, the heat required to raise one mol of these gases one degree in temperature or what is the same thing the product of their molecular weights into their specific heats, MCp, are, within the experimental error in determination, the same for all of them. Similarly, the molal heat capacities of SO_2 and CO_2 are identical, and the same is true of the halogens, etc. These are shown graphically as a function of the temperature in Fig. 1, p. 10.[1]

In the chemical literature, specific heat data are generally given as a function of the absolute temperature on the centigrade scale. Since the specific heat of a substance is the ratio of the heat required to change the temperature of a unit weight of the substance one degree to the heat required to change the temperature of water one degree, all units being the same in comparison, it is seen that specific heat has no units. However, if the specific heat is a function of the temperature such as $a+bT_K+cT^2{}_K$,

[1] These curves apply at moderate pressures, and are based on the equations of Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

Monatomic gases	$MC_p=5.0$
N_2, O_2, CO, NO, halides	$MC_p=6.50+0.001T_K$
H_2	$MC_p=6.50+0.0009T_K$
CL_2, Br_2, I_2	$MC_p=7.4+0.001T_K$
H_2O, H_2S	$MC_p=8.81-0.0019T_K+0.00000222T^2_K$
CO_2, SO_2, N_2O	$MC_p=7.0+0.0071T_K-0.00000186T^2_K$
NH_3	$MC_p=8.04+0.0007T_K+0.0000051T^2_K$
CH_4	$MC_p=7.5+0.005T_K$

In these equations T_K is in degrees Kelvin. Unless extremely high precision is desired, or where pure hydrogen is being considered, its molal heat capacity may be considered the same as that of the other diatomic gases.

where T_K is in "°K.", and it is desired to express it as a function of temperature on some other scale, such as °R.[1], b is divided by 1.8 and c is divided by the square of 1.8. As the molal heat capacity is the specific heat times the molecular weight, what has been said above in reference to specific heat applies also to molal heat capacity, because the molecular weight is also a

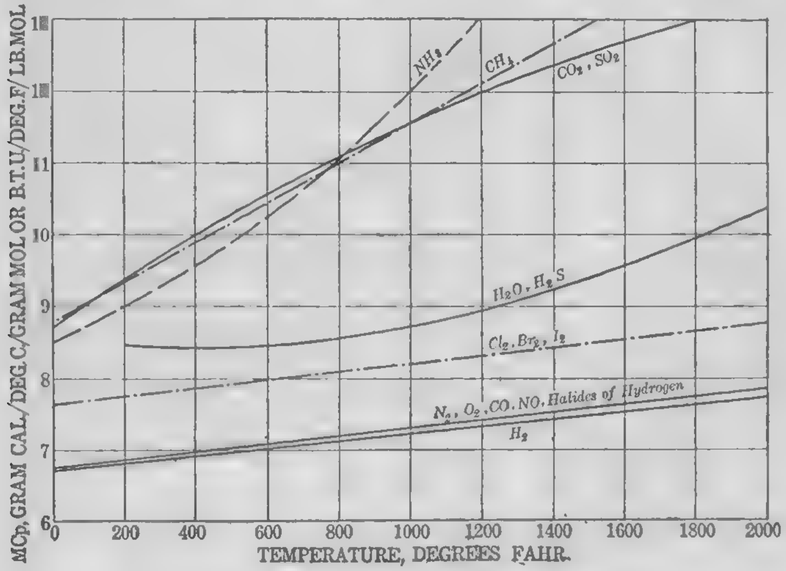


FIG. 1.—Molal Heat Capacities of Gases.

ratio. Thus the molal heat capacity of carbon dioxide, expressed as a function of the temperature where T_K is in degrees Kelvin is

$$MCp = 7.0 + 0.0071T_K - 0.00000186T_K^2,$$

becomes where T_R is in degrees Rankine,

$$MCp = 7.0 + 0.0039T_R - 0.000000574T_R^2.$$

It requires more heat to raise the temperature of a gas at constant pressure than at constant volume, because of the additional energy required to create the larger volume. But the difference in the molal heat capacity of a gas under the two conditions is constant for all gases obeying the gas laws. Numer-

[1] °R means degrees Rankine, namely (°F.+460), not degrees Reamur; °K means degrees Kelvin, °C.+273.

ically this difference is equal to the gas constant R, which when expressed in heat units is 1.985, and is independent of the system of units employed.

Liquids.—While no definite relationship is available for correlating the heat capacity data for liquids, it is interesting to note that the molal heat capacities (and likewise the specific heats) increase with rise in temperature, as shown in Fig. 2.[1]

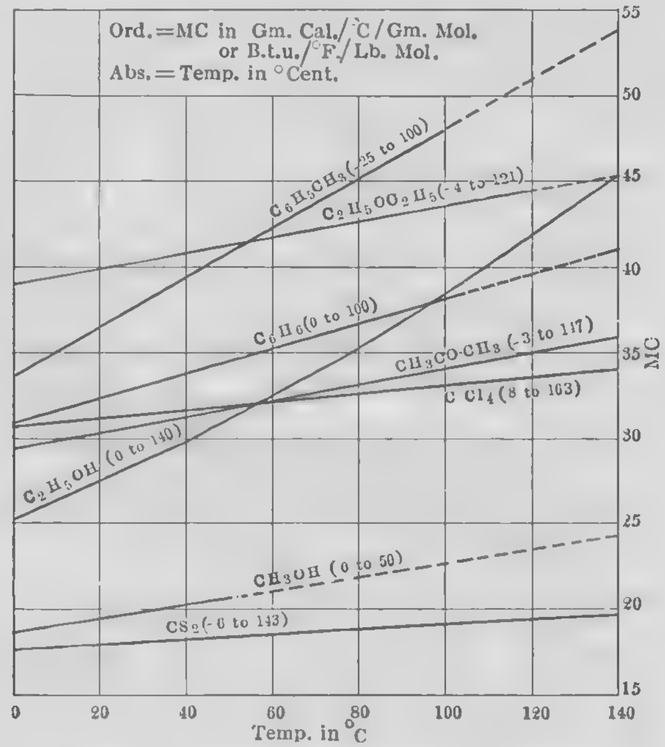


FIG. 2.—Molal Heat Capacities of Liquids.

Solids.—For solids, the Law of Dulong and Petit and the Law of Kopp are sometimes useful in estimating heat capacities of substances. The former states that atomic heat capacity of all solid elementary substances is a constant and the average value is 6.2 at room temperature, although some elements, notably carbon, boron and silicon deviate widely from this. Furthermore, these heat capacities vary with the temperature, in most cases increasing as temperature rises, as shown in Fig. 3.[1] Kopp's

[1] Data taken from the literature.

law states that the formal heat capacity (*i.e.*, the heat capacity of a formula weight of the substance) is an additive function of the atomic heat capacities of the constituent atoms. The following are the atomic heat capacities at room temperature of the elements *in solid compounds*. C=1.8; H=2.3; B=2.7; Si=3.8; O=4.0; P=5.4; F=5.4; all other elements 6.2. For example, the formal heat capacity of pure limestone ($CaCO_3$) would be 6.2+1.8+3×4=20.0 as against an observed value of 20.2.

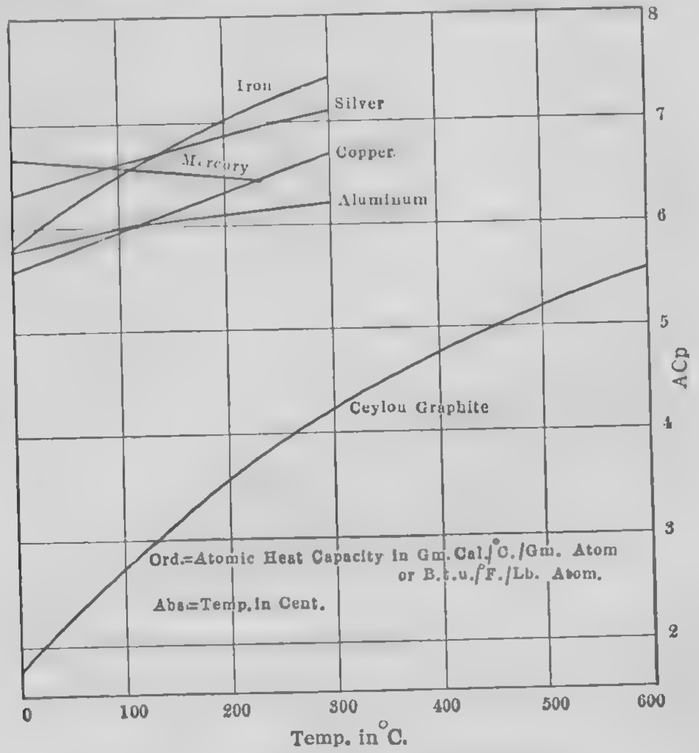


FIG. 3.—Atomic Heat Capacities of Metals.

The specific heat would then be 0.20. These values are, of course, empirical constants and deviations of 10 per cent from the results calculated and those observed are not uncommon.

Molal Sensible Heat Content of Gases.—Because of the variations of heat capacities with the temperature it is often convenient [1] to use curves showing the total molal heat content

[1] The use of such curves is quite an advantage in the case of gases such as steam and carbon dioxide, the heat capacity of which varies according to both the first power and the square of temperature. In order to get the correct value of the heat change per mol it is necessary to integrate these complex equations with respect to temperature. Such integration is the basis of the sensible heat chart described, which is merely a plot of the value of the integral, namely the heat content as B.t.u. per lb. mol above 32° F.

of gases at different temperatures, *i.e.*, the heat required to raise one mol of the gas from an arbitrary zero point (0° C. or 32° F.) up to the temperature in question. These are plotted on logarithmic paper, because this gives constant percentage precision throughout the scale. Two plots are given; in Fig. 4, the

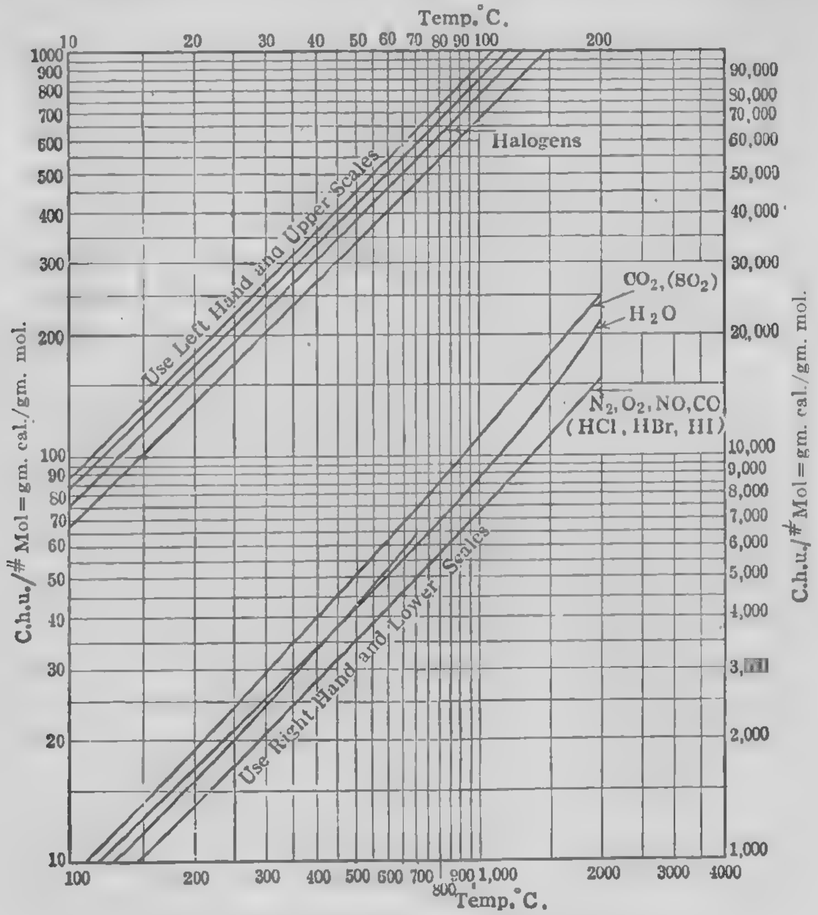


FIG. 4.—Sensible Heat Content of Gases, C.h.u.

co-ordinates are gm. cal. per gm. mol and °C., in Fig. 5, B.t.u. per lb. mol and °F. The accuracy of plotting the calculated values is within 2 per cent. Taking carbon dioxide as an example, the heat required to raise one mol from 70° F. to 900° F. is found

by subtracting the heat content at 70° F. (which from Fig. 5 is 338 B.t.u.) from that at 900° F. (which is 8750 B.t.u.) giving 8412 B.t.u. per lb. mol. As a matter of interest, the true mean molal heat capacity of CO_2 over this range is $8412/830 = 10.14$ B.t.u. per lb. mol, and the true mean specific heat is $10.14/44 = 0.2305$.

Molal Heat of Vaporization.—Another molal relationship which is often of value where exact data are wanting is that known as

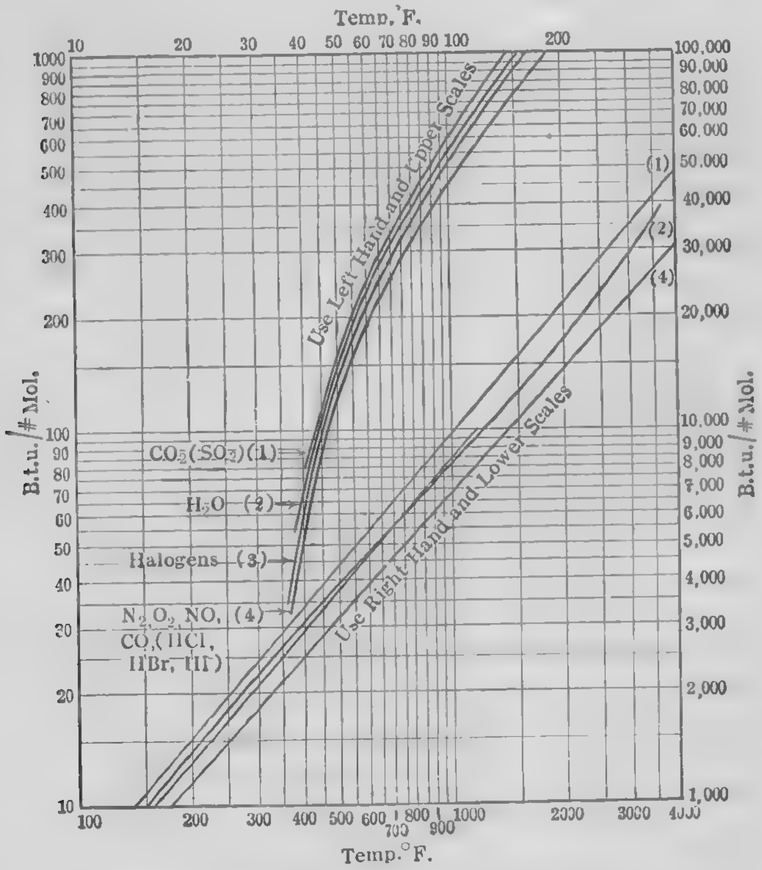


FIG. 5.—Sensible Heat Content of Gases, B.t.u.

Trouton's rule. This states that the molal heat of vaporization (Mr), of the liquid at its absolute boiling point, T, gives a ratio, Mr/T, which is of the same order of magnitude for all liquids. In the above ratio M designates molecular weight, r, the heat of vaporization per unit weight of the liquid, and T the boiling point on the absolute temperature scale. In the French system of units one expresses heat of vaporization as gram calories per gram

of substance and absolute boiling point as degrees Centigrade absolute, while in the English system the heat of vaporization is expressed in B.t.u. per lb. of substance and the absolute boiling point in °F. absolute. Thus it is seen that the ratio Mr/T is numerically the same using either set of units, since gram calories per gram mol per °C. absolute is the same as B.t.u. per lb. mol per °F. absolute. The variations from Trouton's rule are in some cases large and it is, as noted, limited to heat of vaporization at the boiling point *at atmospheric pressure.*

A better approximation, and one which is not limited to the boiling point at atmospheric pressure, is a variation[1] of the rule of *Hildebrand.* This states that Mr/T is a function of the molal concentration of the vapor evolved. The molal heats of vaporization of water at 373° C. abs.(1 atm.) and at 453° C. abs. (10 atm.) are known to be 9720 and 8670 gm. cal. per gm. mol respectively, and hence the corresponding values of Mr/T are 26.0 and 19.1. Calling the pressure at the temperature in question p atm., the corresponding molal concentrations are proportional to $1000p/T$, namely 2.68 and 22.1 in these cases. It will be seen that these values lie on curve 1 of Fig. 6,[2] and a curve determined in this manner may be used to predict the molal heat of vaporization of water at other temperatures. Extrapolation becomes uncertain, however, in the neighborhood of the critical pressure, as shown by the dotted portion of curve 1. Curve 4, based on data for carbon tetrachloride, checks the limited data available for paraffin hydrocarbons at atmospheric pressure, and is valuable in estimating the latent heats of vaporization of the various fractions obtained in the refining and cracking of petroleum.[3]

[1] W. K. LEWIS and H. C. WEBER, *J. Ind. Eng. Chem.*, **14**, No. 7 (July, 1922), 485.

[2] W. H. MCADAMS and J. C. MORREEL, *Ind. Eng. Chem.*, **16**, No. 4 (April, 1924), 375.

[3] The average molecular weight of the fraction may be taken with sufficient precision as corresponding to that of the normal alipathic hydrocarbon boiling at a temperature equal to the average boiling point of the hydrocarbon mixture under consideration. The relation between the molecular weight M of any normal paraffin hydrocarbon and its atmospheric boiling point t, expressed in degrees Centigrade, is given by the equation: $\log_{10} M = [2.51 \log_{10}(t+393)] - 4.7523$.

Vapor Pressure of Liquids.—In many cases it is necessary to interpolate or extrapolate the curve of vapor pressure *versus* temperature. The method proposed by Cox[1] is quite helpful. A straight line is drawn at a convenient angle on co-ordinate paper. The vapor pressures of water are then plotted on a logarithmic scale, allowing the corresponding temperatures to determine the temperature scale, as shown on Fig. 7 by the dotted line marked "Steam." Using these coordinates, data for various paraffin hydrocarbons are plotted, giving substantially straight lines. Since the latter intersect at a common point, one experimental point is sufficient for the estimation of the vapor-pressure curve of any normal paraffin hydrocarbon.

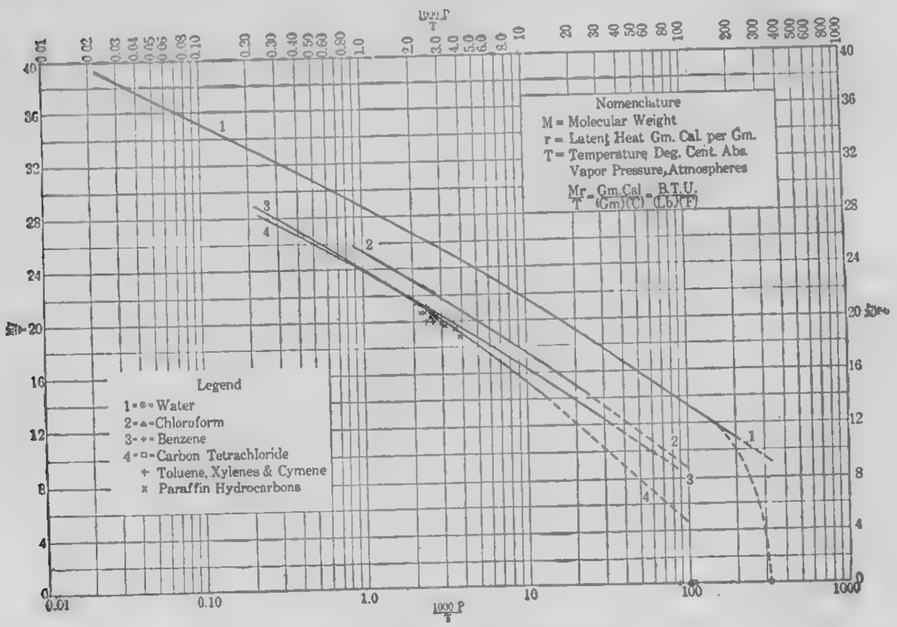


FIG. 6.—Hildebrand Function.

GENERAL DISCUSSION OF STOICHIOMETRIC PROBLEMS IN APPLIED CHEMISTRY

Types of Operation.—The operations or processes of applied chemistry can be classified under three heads: intermittent, continuous, and a combination of these two, or semi-continuous.

[1] E. R. Cox, *Ind. Eng. Chem.*, **15**, No. 6 (June, 1923), 592; see also CALINGAERT and DAVIS, *Ibid.* (December, 1925), 1287.

Illustrations of an intermittent process are the burning of brick and pottery in the older type of kiln in which, after firing, the whole is allowed to cool for discharging and refilling; the production of coke in beehive ovens; the pot process for the production of nitric acid from Chili saltpeter and sulphuric acid; the recovery of oil from seeds in hydraulic presses; and the like. Typical of continuous processes are the chamber production of sulphuric acid from sulphur, the extraction of light oils and ammonia from

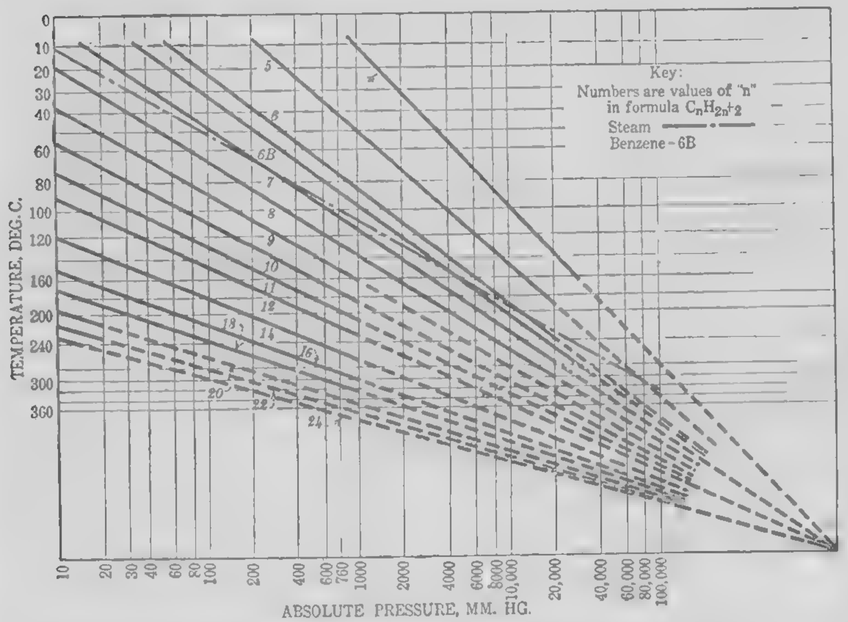


FIG. 7.—Cox Chart for Extrapolating Vapor Pressure-temperature Curves.

illuminating gas by solution in suitable solvents, the operation of continuous stills and dephlegmating columns for the separation of volatile solvents, etc. Continuity of operation offers such obvious and marked advantages that it is used wherever practicable; but in many cases continuity can only be approximated, giving rise to semi-continuous operations, as in the intermittent firing and cleaning of a hand-fired boiler, the operation of a "ring" furnace, the manipulation of the leaching tanks in the extraction of black ash or tan bark, the charging of a blast furnace, and the like. Where the character of the operation is

essentially intermittent, continuity is often approached by the combination of a number of units operating simultaneously but in different stages, as in the coking of coal in by-product ovens, and the recovery of waste heat in regenerative chambers of refractory checker work (*e.g.*, blast furnace stoves). While this last class can be treated as semi-continuous if the whole process, made up of the combination of all the unit operations, is under consideration, it must be classified as intermittent when one is dealing with the individual unit operation.

Those chemical reactions in which a single substance is transformed into another single substance are comparatively rare. On one or both sides of the reaction equation there usually appears more than one substance. Most chemical operations can therefore be conceived as made up of diverging, converging, or crossing and intermingling streams of flow. *Diverging streams* are illustrated by the electrolysis of a salt solution to form caustic, chlorine, and hydrogen; of water (containing caustic) to produce hydrogen and oxygen; in the separation of mixtures of volatile liquids by distillation (alcohol and water; benzol and toluol, etc.); by the destruction distillation of wood, coal, and the like. In each case one stream or substance enters the process to leave by several streams *diverging* from it. Illustrations of *converging streams* are found in the production of vulcanized rubber by the compounding and curing of raw rubber with sulphur and other admixed materials; in the combustion of gaseous fuels, etc. Here two (or more) substances enter the process to combine or *converge* into one substance and thus leave by a single stream. The combustion of coal with air to form flue gases and ash, the reduction and liquefaction of iron in the blast furnace, and the roasting of sulphide ores with air to form metallic oxides and eliminate the sulphur are typical of *crossing streams;* and in these cases, several streams enter into an operation, suffer chemical combination and transformation, or, in other words, *cross* and leave by several entirely different streams.

Balance of Material Involved in an Operation.—In the quantitative calculation of problems in applied chemistry it is advisable to start with the following equation:

Total Input = Total Output + Accumulation, or its equivalent,
Total Input + Depletion = Total Output,

accumulation and *depletion* referring to increase or decrease of material in the system itself. This equality may be applied to a single unit operation, or to a whole process made up by the combination of any number of unit operations. It may be applied separately to each element entering into the operation or process, for which data are available; and when so applied to a number of elements, the equation for each element is not equivalent to, but is independent of, the others, provided the data for that element were independently obtained. It may be applied to the energy relations of the systems, and in this form gives another independent equation. It may be applied to the input and output of matter as a whole, but this last is obviously not an independent expression, being merely the sum of the equations for the various elements. The use of this principle is observed in nearly every illustrative problem.

In these equalities the only awkward factors are the terms *accumulation* and *depletion* in the system itself. These can of course be determined, but usually with some difficulty. They can, however, almost always be eliminated by proper choice of data and method of calculation. In the great majority of cases in industrial practice intermittent operations are repeated in cycles which recur a relatively large if not an almost indefinite number of times, and both continuous and semi-continuous operations function steadily over long periods. The possibility of accumulation or storage of materials or energy in a system or apparatus is necessarily limited, and it is usually possible to control the amounts in process without much difficulty. If now the above equalities be applied over a period of time such that the maximum possible fluctuations of amounts in process are known, from the nature of the operation and apparatus, to be negligible in comparison with the input and output for the time period chosen, then the terms for accumulation or depletion may be dropped, giving, Total Input = Total Output. This is perhaps more conveniently written,

Total Input = Useful Output + Losses, or more simply,
Input = Output + Losses.

These equations are used for two main purposes; first, in testing existing apparatus and operations to determine the actual performance, and second, in designing new apparatus and in planning new operations for future installation and service. This chapter deals primarily with the first of these functions, that is, with the methods used to secure data and information which will give insight into the present or past operation of an apparatus, but the methods employed can be generally used in the design of new equipment, as will be developed later.

Efficiency.—The present performance of an apparatus is determined not only by its capacity but by its efficiency and since there can be different kinds of efficiencies, accurate definition of the term is essential. Thus there can be at least two heat efficiencies, defined as the heat utilized by an apparatus divided by its heat input, or as the heat utilized divided by that theoretically capable of utilization. There is also the chemical efficiency which may be applied to each chemical element in the process. An example of the chemical efficiency of a process is given in the crystallization of a salt; of the impure salt used, there are 1000 lbs. of the pure substance, in the output there are 600 lbs. and there are left 380 lbs. of recoverable salt in the wash water and mother liquor. As efficiency is generally defined as output/input, that of this process would seem at first to be $\frac{600}{1000}\times 100 = 60$ per cent, yet since a large amount of the apparent losses are entirely recoverable and would be in practice, it is hardly fair to charge this process with such a low efficiency. Therefore the chemical efficiency should be defined as the output/input, where by net input is meant that amount of material which would have to be put through the process in order to get the *same* output. The efficiency is then $\frac{600}{1000-380}\times 100 = 96.8$ per cent. The 380 lbs. is subtracted from the 1000 lbs. because only 620 lbs. would have to be used to get an output of 600 lbs. if the 380 lbs. were recovered. The reason the 380 lbs. are not added to the 600 lbs. is because the output would be changed and the input of 1000 lbs. would also have to be changed to meet the new output.

Test Period.—The choice of what may be termed the *test period*, *i.e.*, the length of time during which data as to input and output must be taken in order to render negligible any accumulations or depletions in the system itself, must depend on the conditions of each individual case, and can usually be estimated easily. In intermittent operations, the test period should be at least one complete cycle, and in those cases in which a certain amount of material is left in process from cycle to cycle, as in soap-boiling, must be more than a single cycle. Where practicable it is always desirable to cover a number of cycles to eliminate individual variability. In continuous processes the test period can be the shorter the more uniform the operation, and the less the material in process. Semi-continuous operations and processes should, if possible, be followed over a time period sufficiently long that they may be considered as practically continuous. Thus a boiler test must extend over a period of about thirty-six hours, in order to eliminate errors due to variations in the amount of fuel in the firebox at the beginning and end of the test. If test periods of adequate length cannot be provided, correction must be made for variations of amounts in process.

Choice of Data to be Secured and Used.—If a test actually includes the measurements of every item of input and output, then the use of the given equalities (p. 19) serves merely as a check upon the accuracy of the measurements. Usually, however, these relationships are employed to lessen the amount of data to be collected and the number of measurements to be made, without sacrifice of any information obtainable from the test. Measurements are restricted to those made easily and with precision, other quantities, which could be directly determined only with difficulty, being calculated. For example, without the installation of very special equipment, it would be difficult to measure the air consumption and the volume of the flue gases in a boiler test, while it is easy to measure the coal actually burnt and the water evaporated. The first two quantities are therefore calculated by use of the above equalities from the other data collected. In testing practice it is unwise to restrict the measurements taken to the minimum necessary for the calculations required. All data which can be secured with reasonable effort should be recorded, because any excess may be used to furnish desirable checks on the accuracy of the other observations.

In order to get a complete determination of the balance of the elements in any operation, the amount and composition of each stream entering and leaving the system must be measured. This requires the determination of the quantity and of the analysis of

each stream. Since, however, an independent expression can be set up involving equality of input and output of each element, for each such equation formulated it is allowable to omit from the above one measurement, either of quantity or of composition. As already indicated, the measurements to be omitted should be so chosen that those measurements which are actually taken will be accurate and easy to make. Because analytical determinations are usually easier than large-scale measurements of quantity, the former are generally employed to evaluate the latter. However, it is always necessary to make at least one direct measurement of quantity in order to determine the capacity of any system.

In making calculations of this sort care must always be observed to avoid the possibility of gross error in the result due to insufficient accuracy in the measurements made. For example, a quantity, obtained by subtracting two other quantities nearly equal, may itself be very inaccurate, if relatively small errors in the two latter happen to be of opposite sign. The data to be taken experimentally should be chosen with this point in mind.

Sampling.—In securing analytical data in connection with industrial processes the necessity for proper methods of sampling cannot be over emphasized. It is useless to waste time in the laboratory carrying out an analysis if the sample is not truly representative of the stream from which it was taken. Indeed, worse than this, analytical results on non-representative samples may lead to false conclusions.

To be representative a sample should be collected (as nearly as may be) continuously during the test period. Where possible the amount of sample withdrawn should be proportional to the volume of the stream at each point of time. The sample should be withdrawn not at one point in the stream but at a number of points well distributed over its cross-section except in those cases where the stream is known to be uniform (*e.g.*, a gas that has traveled some distance or around a number of obstructions). These conditions imply the collection of large samples and these must be sub-divided before analysis. It is not difficult to get complete mixing of a large sample of gas or homogeneous liquid and the removal of the ultimate sample for analysis involves no difficulty.

The sampling of solid materials is an entirely different problem. Because of the tendency of the large lumps of the solid to separate from the fine material the sample must be crushed before sub-

division (quartering). Even thus a satisfactory analytical sample can be obtained only by successive sub-divisions with most thorough mixing before each successive quartering. The largest individual particle in the mass must be extremely small compared with the sample before quartering is undertaken. It is frequently difficult to reduce the whole original sample to a powder and to meet this requirement in such case the sub-division must be re-ground as the sample gets progressively smaller. Mechanical samplers are on the market and are desirable because they reduce the human element in collecting the sample.

General Methods of Calculation.—There are certain practical suggestions and methods which, while theoretically adding nothing to the preceding generalizations, are none the less worth mentioning. These are in the nature of tricks in computation, which, in many special cases, simplify not only calculations but sometimes experimental work as well.

It frequently happens that some one element taking part in a chemical operation enters solely by one stream and leaves solely by another. This is true, for example, of the sodium in the electrolysis of salt, of the nitrogen in a blast furnace, and for all practical purposes of the nitrogen in the combustion of coal. It is obvious that, if the quantity of one of these streams be known, the amount of the other can be obtained directly from analysis of the two for this one element. Furthermore, if the analyses of the two streams be complete, the quantities of all other elements present in each of them can at once be calculated. This idea is utilized by illustrative problems on pp. 28 to 35.

Where an element enters and leaves mainly by a single stream, the same method is advantageously employed, merely correcting for divergencies. Thus, in the furnace combustion of coal, the carbon enters mainly in the solid fuel, the amount of which is measured and the carbon content determined by analysis. The carbon leaves mainly in the flue gas, that small portion remaining in the ash as unburnt combustible being determined and correction made for it. This gives immediately the amount of the flue gas. The nitrogen of the flue gas coming mainly from the air (the nitrogen of the fuel is usually negligible in comparison), one can immediately calculate the quantity of air used for combustion. It will be noted that the carbon and the nitrogen are used to determine the ratios of the volumes of corresponding ingoing and

outgoing streams. The use of single elements or components for such a purpose is often possible, and offers marked simplification in calculation.

The stoichiometric relations known to exist from the nature of the reactions taking place in a given case often greatly simplify the problem, and make possible important quantitative deductions. Thus the analysis of a flue gas from the combustion of coal shows certain amounts of CO_2, CO, O_2 and N_2. Since practically all the N_2 came from the air, one can directly obtain the amount of O_2 that came with it. The total O_2 shown by the flue gas analysis, including both free and combined, is always *less than that entering in the air*. From our knowledge of the chemical composition of coal, we know that almost the whole of this deficit must have been used up in the combustion of hydrogen in the fuel. This difference between oxygen corresponding to the nitrogen and oxygen appearing in the analysis [1] must, therefore, correspond to and be a measure of the *combustible* hydrogen in the coal. The analysis of the flue gas is in this case in a very real sense equivalent to an analysis of the fuel itself. (See illustrative problems on pp. 28 to 33.) While such definite reaction relationships are of the greatest value where they exist, there are many cases where the number of possible side reactions is so great and the extent to which they take place so uncertain that the stoichiometric relationships implied in the chemical equations lose much of their utility. This is very likely to be the case in organic reactions, but even in inorganic problems it is imperative to formulate and in the calculations to provide for all side reactions which can appreciably affect the result. These limitations must not, however, make one fail to use these relationships where really applicable.

As in stoichiometric calculations in analytical chemistry, it is unnecessary that the chemical equations employed correspond to the exact mechanism of reaction. Any combination of the actual

[1] It must be kept in mind that a gas analysis in which the gases are kept saturated with water vapor whenever measurements are made (as is almost universally done) automatically eliminates the water vapor from the results, and gives directly the composition of the water-free gases. The reason for this is, that although the volume of the gases is increased by the presence of the water vapor, the increase is at all times the same fraction of the total gas volume. It is as though the analysis were carried out at a pressure lower than that actually used by an amount equal to the constant vapor pressure of the water. See also page 226.

reaction steps, even though eliminating intermediate but compensatory stages, can be used; *e.g.*, reactions in aqueous solutions need not be written in ionic form in the calculation of quantities of precipitates, volumes of solutions, and the like.

Basis of Calculation.—It is comparatively seldom that a complete balance of input and output is made in connection with an industrial operation or process, but much more frequently interpretation of partial results is desired. Usually these results are the analyses of different streams. Such analyses are almost never directly comparable, as will appear in a complete balance of input and output, and direct comparison may lead to gross error. This is because analyses are usually reported in per cent of the stream in question, and it is obvious that analysis alone cannot show the relation between the *volume* of that stream and that of any other.

An illustration will make this point clear. A drier is delivering one ton an hour of a product containing 20 per cent of water. The wet charge entering the apparatus for drying carries 60 per cent of water. How many pounds of water are evaporated per hour? The first impulse may be to say that the water decreases from 60 to 20 per cent, that is, by 40 per cent. But the first two figures have no direct relation to each other, because they do not refer to a common basis. The weight of material entering, of which water is 60 per cent, is greater than the 2000 lbs. of material leaving. It is believed that difficulties of this sort are best avoided by reducing the analytical results to a common basis in order that direct comparison may be made. Where, as in the case cited, there is a common component which both enters and leaves by a single stream, and there is no accumulation or depletion of that component during the process, the amount of that component passing through the operation in a given time must be the same in both analyses, and hence may serve as a constant basis of comparison. This unidirectional component is, in this case, the dry material itself. If, therefore, the analytical results be expressed as ratio of water to dry material, *i.e.*, 0.25 in the dried product and 1.50 in the wet, the difference, 1.25 truly represents the water evaporated per pound of dry material. Since the dry material is 80 per cent of the product or 1600 lbs. per hour, the evaporation is 1.25 times this, or 2000 lbs. per hour.

The concept of the preceding paragraph may be expressed by

the following rule: Where there are unidirectional elements or components in an operation, express compositions (*i.e.*, analyses) as ratios to these elements.

It must be admitted that the method just outlined, in cases where the flow of all components is complicated, becomes very involved. However, it is so frequently applicable, and where applicable is so direct, that it is advisable to form the habit of using it.

To be sure this same problem may be solved without recalculation of the analytical data to a new basis. Call y the weight of wet material entering the drier. Equate input of dry material to output.

$$0.40y = 0.80\ (2000)$$

whence $y = 4000$

Evaporation = loss in wt. = 4000 − 2000 = 2000 lbs.

The basis of such a calculation involves the concept not only of quantity but also of time. For example, in the preceding calculation the time basis was one hour. The time basis of calculation may be the duration of a test, or any convenient unit. Frequently the time basis may be implicit, and its actual value unknown, *e.g.*, the time necessary to produce a certain quantity of product or to consume a certain amount of raw material.

Not infrequently one must, at the start of the computation at least, employ two or more bases, but effort should always be directed to reducing them to a common basis. Indeed, when an analysis is reported in per cent, it represents the arbitrary choice as a basis of 100 parts of the particular substance, or stream, analyzed, and inferentially the acceptance as a time basis of the period required for the development or passage of 100 parts of that particular stream.

When one is dealing with crossing streams, it often occurs that some element or component passes from one stream to the other, either completely or in part; such an element can be made the basis of computation for determining the ratio between the two streams. For example, in the blast furnace a stream of solids, the composition and amount of which is known from the records of the furnace ordinarily kept, flows down through the furnace and out as two separate streams of slag and pig iron. Up through the furnace flows a stream of air, leaving as tunnel-head gas.

The ratio of air to tunnel-head gas is determined by the nitrogen, the common component. The ratio of charge to pig is similarly determined by the iron. The ratio of these two streams to each other can be determined by either carbon or oxygen, both of which pass from the charge to the gas stream. If carbon be used, allowance must be made for carbon left in the pig, as found by analysis; if oxygen be employed, that entering in the air, and that in the unreduced part of the charge must be taken into account.

It is advisable to write at the head of the computation the basis employed, to indicate clearly change to a new basis, transformation from one basis to another, and the ratios by which such transformations are effected. Tabulation of figures is a great help towards brevity and clearness.

Missing Data.—Finally, it must be pointed out that the calculations of applied chemistry often require the making of assumptions and approximations. In industrial work it is frequently impracticable, on account of inconvenience, expense or interference with plant operation, to make all the measurements necessary for a complete determination of the quantities which it is desired to evaluate. In such cases it is the part of good judgment not to give up, but to make wisely such simplifying assumptions as are justified by the conditions, and on these, utilizing data already available and such as can readily be obtained, base a quantitative estimate, always keeping in mind the limitations in accuracy imposed by the assumptions made.

General Procedure in Solving Problems.—In the solution of problems the following steps will be found helpful:

1. Sketch a diagrammatic flow sheet of the process.
2. Write the chemical equations involved.
3. Indicate the basis (or bases) of calculation.
4. Tabulate the data, and the intermediate steps in calculation.

In simple cases the formal writing out of the first two may be omitted.

The application and utility of certain of the general principles outlined above is illustrated by the three problems following; the first concerns the combustion of fuel oil, while the other two relate to the production of sulphur dioxide gas by burning sulphur with air, and the absorption of the sulphur dioxide in milk of lime. Additional illustrative problems are given on pp. 241 to 245.

Illustration I.—A boiler furnace burns fuel oil with dry air at 40° F. and at a barometric pressure of 30.1 in. of mercury. The average Orsat analysis of the flue gas is 12.9 per cent CO_2, 3.8 per cent O_2, and 83.3 per cent N_2, and the temperature of the flue gases at the base of the stack is 560° F. Assuming [1] the oil to contain only carbon and hydrogen, calculate:

(1) per cent excess air,[2]
(2) the wt. per cent of carbon in the oil,
(3) cu. ft. of air per lb. of oil,
(4) cu. ft. of flue gas entering the stack per lb. of oil, and
(5) the partial pressure of water vapor in the stack gases.

Solution.—(1) Since the analysis of this particular fuel oil is unknown, the oil cannot conveniently be made the basis of calculation. The analysis of the flue gas is known and can therefore be made the basis. Consider 100 lb. mols of the flue gas as analyzed, *i.e.*, on the *dry basis*.[3] For the purpose of calculation the distribution of the individual elements may be taken as shown in the following tabular form:

Gas	Mols	Atoms C	Mols O_2	Mols N_2
CO_2	12.9	12.9	12.9	
O_2	3.8	.....	3.8	
N_2	83.3	.....	.....	83.3
Totals	100.0	12.9	16.7	83.3

It is seen from the above that the ratio of total O_2 to N_2 in the flue gas (16.7/83.3) is less than that in the air (20.9/79.1). This is due to the fact that part of the oxygen coming from the air has united with the hydrogen of the oil to form water vapor, which does not show in the Orsat analysis.

Neglecting the small amount of nitrogen in the oil, as indicated above, all the N_2 in the flue gas must have come from the air, hence, the air used is $83.3/0.791 = 105.2$ mols. (Thus, a "nitrogen balance" is used to determine the air used.)

Since the dry air contains 20.9 per cent O_2 by volume, the O_2 entering the furnace amounts to $(0.209)\ (105.2) = 22.0$ mols. But the total O_2 in the dry

[1] This assumption has been made to simplify the calculations. The oil actually contains a small percentage of nitrogen, sulphur, ash, etc., but it can be shown that the above assumption introduces little error. This is because the volume of the nitrogen coming from the oil is so small relative to that of the nitrogen from the air used. Similarly, the nitrogen in coal, coke, and wood may be neglected without serious error. In the case of the combustion of producer gas, the nitrogen cannot be neglected without introducing a considerable error.

[2] This will be discussed further in the chapter on "Combustion."

[3] See p. 24.

flue gas is 16.7 mols, hence the difference, 22.0 − 16.7, or 5.3 mols of O_2 has disappeared to form 10.6 mols of water vapor, thus burning 10.6 mols of hydrogen. (Thus, an "oxygen balance" is made to determine the oxygen used in burning hydrogen.)

"Percent excess air" refers to the air used in excess of that theoretically needed for complete combustion, compared to that theoretically needed for perfect combustion. If one deals with O_2 coming from the air, excess air may be interpreted in terms of "O_2" instead of "air," and this is convenient. The unnecessary O_2 from the air per 100 of necessary O_2 from the air may be calculated in several different ways:

$$\frac{\text{unnecessary}}{\text{total}-\text{unnecessary}} = \frac{(3.8)\ (100)}{(22.0-3.8)} = 20.9 \text{ per cent,}$$

$$\frac{\text{unnecessary}}{\text{necessary}} = \frac{(3.8)\ (100)}{(12.9+5.3)} = 20.9 \text{ per cent, or}$$

$$\frac{\text{total}-\text{necessary}}{\text{necessary}} = \frac{[22.0-(12.9+5.3)]\ (100)}{(12.9+5.3)} = 20.9 \text{ per cent.}$$

It will be noted that these are not independent methods but merely various arrangements of the same figures.

(2) Since the weight of the oil equals the weight of the carbon (12.9)(12) plus the weight of the hydrogen (10.6)(2.02), the per cent carbon by weight in the oil is readily calculated:

$$\frac{(12.9)\ (12)\ (100)}{(12.9)\ (12)+(10.6)\ (2.02)} = \frac{(154.5)\ (100)}{154.5+21.4} = 87.9 \text{ per cent.}$$

This figure is not required in further calculations, but it serves as a rough check on the accuracy of the flue gas analyses, since it should compare well with that usually found in fuel oils, as it does in this case. In passing, it should be noted that the atomic ratio of carbon to hydrogen found, $12.9/(2)\ (10.6) = 0.609$, is higher than $\frac{1}{2}$, showing that the oil contains carbon in excess of that indicated by the formula $(CH_2)_n$.

(3) Since the weight of oil is 175.9 lbs. and the dry air on this basis is 105.2 mols, the air used per lb. of oil may be readily calculated:

$$\frac{105.2}{175.9} \left| \begin{matrix} \text{Mols air} \\ 359 \end{matrix} \right| \left| \begin{matrix} \text{Cu. ft. at S.C.} \\ 160 \mid 10 \\ 160 \mid 32 \end{matrix} \right| \left| \begin{matrix} \text{At 40° F., 29.9 in.} \\ 29.9 \\ 30.1 \end{matrix} \right| = 217 \text{ cu. ft. per lb. of oil}$$

(4) The mols of flue gas entering the stack will contain the 100 mols of dry gases (CO_2, O_2, and N_2) plus the 10.6 mols of water vapor, a total of

110.6 mols of wet flue gas. The volume of stack gases per lb. of oil is calculated as follows:

Mols flue gas		Cu. ft. at S.C.	At 560° F., 29.9 in.	
110.6	359	460+560	29.9	=465 cu. ft. per lb. of oil
175.9		460+32	30.1	

(5) The partial pressure of the water vapor in the stack gases is readily calculated, remembering Dalton's Law:

$$p = 30.1 \frac{10.6}{110.6} = 2.88 \text{ in. of mercury.}$$

Illustration 2.—The gas from a sulphur burner shows on analysis 17.4 per cent SO_2 and 2.7 per cent O_2. The air enters the burner at 60° F., and the gas leaves it at 760° C. The gas is now cooled to 70° F. in a lead pipe cooler, using cooling water at 58° F., which rises to 90°. The sulphur burnt is 99.4 per cent pure, and the hourly consumption is 680 lbs. Neglect any moisture in the entering air, and assume barometer to be normal.

(1) What is the amount of SO_2 leaving the burner in lbs. per hour?
(2) What is the air consumption in cu. ft. per min.?
(3) What is the volume of gas leaving the burner and the cooler in cu. ft. per min.?
(4) What is the heat dissipated from the burner in B.t.u. per hour?
(5) What is the water consumption of the cooler in gals. per hour?

Solution.—Turning attenton first to the gas analysis, it must be borne in mind that any SO_3 formed during the combustion does not show up in the gas analysis, being condensed and removed as H_2SO_4 by interaction with either the moisture in the original air, or the water used to saturate the gas sample prior to analysis. Furthermore, it is a convenience to imagine the analysis applied, not to the small sample originally taken, but to 100 mols of the gas.

Basis: 100 Mols of Gas as Analyzed

Gas	Mols	Mols of O_2 accounted for	Atoms of S accounted for
SO_2	17.4	17.4	17.4
O_2	2.7	2.7	0.0
N_2 (etc.)	79.9	0.0	0.0
Totals	100.0	20.1	17.4

Total O_2 from air (corresponding to N_2) $= (79.9)\frac{20.9}{79.1} = 21.11$ mols.

O_2 unaccounted for in gas analysis $= 21.11 - 20.1 = 1.01$ mols $O_2 \rightleftharpoons \frac{2}{3}$ of $1.01 = 0.67$ mols SO_3 formed.

Since for 17.4 mols SO_2 produced, 0.67 mols of SO_3 are formed, 3.7 per cent of the total sulphur burnt goes to SO_3.

In order to secure the information required, it is now best to adopt the time basis indicated in the questions themselves.

(1) *Basis.*—One hour of operation.

Lbs. crude sulphur		Lbs. S	Mols S	Mols SO_2	
680	0.994	1	(1.0-0.037)	64.07	=1300 lbs. SO_2 per hr.
		32.07			

(2) *Basis.*—One minute.

Lbs. SO_2		Mols SO_2	Mols N_2	Mols air	Cu. ft. at S.C.	
1300	1	79.9	100	359	520	=744 cu. ft. air per min.
60	64.07	17.4	79.1		492	

(3) *Basis.*—One minute.

Lbs. SO_2		Mols SO_2	Mols gas	Cu. ft. at S.C.	
1300	1	100.67	359	273+760	=2658 cu. ft. per min. leaving burner
60	64.07	17.4		273	

The gas leaving the cooler is found by correcting this last result for the temperature change, to be 756 cu. ft. Were moisture present, the SO_3, the volume of which it will be noted was added to that of the gas as analyzed, would condense out at this low temperature as H_2SO_4.

(4) *Basis.*—100 mols gas as analyzed = 100.67 mols total gas (including SO_3).

The heats of reaction may be taken from the data of Berthelot:

$$S + O_2 = SO_2 + 69{,}300 \text{ cal.}; \quad S + 1\tfrac{1}{2}O_2 = SO_3 + 91{,}900 \text{ cal.}$$

The heat evolved is, therefore,

$$17.4(69{,}300) + 0.67(91{,}900) = 1{,}268{,}000 \text{ C.h.u.}$$

The sensible heat carried out by each gas is its total heat per mol at 760° C. less its total heat at 60° F. (15.6° C.) multiplied by its number of mols. (See Fig. 4, p. 13.) The total heat of SO_3 is not available, but there will be no serious error if its molal heat capacity be taken as 10.

HEAT CONTENT[1] OF GAS LEAVING BURNER (C.H.U.)

Gas	Mols	Total Heat		Difference	Product
		At 760° C.	At 15.6° C.		
SO_2	17.4	8100	138	7962	138,600
SO_3	0.67	7600	156	7444	5,900
N_2+O_2	82.6	5400	107	5293	437,200
Total heat remaining in gas					580,800

The heat dissipated in the burners is that evolved (1,268,000 C.h.u.) less that carried out by the gas (580,800 C.h.u.) = 687,200 C.h.u. = 1,237,000 B.t.u. This, however, is per 100 mols of gas as analyzed, or 17.4+0.67 = 18.07 mols sulphur burnt. Since the mols sulphur burnt per hour are $\frac{680(0.994)}{32.07}$ = 21.06 mols, the heat dissipated per hour is

$$(1{,}237{,}000)\frac{(21.06)}{(18.07)} = 1{,}442{,}000 \text{ B.t.u. per hour.}$$

(5) *Basis* = 100 mols of gas as analyzed.

HEAT CONTENT[1] OF GAS LEAVING COOLER (C.H.U.)

Gas	Mols	Total Heat		Difference	Product
		At 70° F.	At 60° F.		
SO_2	17.4	186.5	138.3	48.2	838
SO_3	0.67	211	156	55	37
N_2+O_2	82.6	143.3	106.6	36.7	3030
Heat above 60° F. carried out by gas at 70° F.					3905

[1] Above 60° F.

Since the gas enters the cooler with 580,800 C.h.u. and leaves with 3905, it gives up to the cooling water 576,900 C.h.u. per 100 mols of gas as analyzed, or

$$576{,}900\frac{(21.06)\ (1.8)}{(18.07)} = 1{,}210{,}000 \text{ B.t.u. per hour.}$$

Since the cooling water rises 32°, the hourly requirement is 37,800 lbs. = 4540 gals.

Illustration 3.—The gas from this burner is absorbed in a milk of lime, to form bisulphites, in a tower in which the milk flows counter current to the gas. The gas leaves the tower at 76° F., containing by analysis 2.8 per cent O_2 and no SO_2. The bisulphite liquor produced is 7.05 per cent total SO_2, of which 1.15 per cent is "free," the rest, 5.90 per cent being present as bisulphites. The dolomitic lime used is 82 per cent CaO and 16 per cent MgO.

(1) What is the volume of gas leaving the absorption tower per minute?
(2) What is the consumption of lime and of water to slake it per hour?
(3) How much bisulphite liquor is produced per hour?

Solution.—(1) *Basis.*—One minute.

Cu. ft. air at 60° F.	N_2 at 60° F.		Waste gas at 60° F.	
744	0.791	1.0	536	= 624 cu.ft. of dry gas per min.
		(1.0-0.028)	520	

It must, however, be remembered that this gas is saturated with water vapor (the vapor-pressure lowering of water in a saturated lime solution being negligible). The partial pressure of the water vapor is, therefore, 22.7 mm., whence the total volume is

$$624\frac{(760)}{(760-22.7)} = 643 \text{ cu. ft.}$$

(2) There is available the analysis of the gas entering the tower and of that leaving it. The nitrogen in this gas is practically unchanged; it could disappear in no way other than by solution in the bisulphite liquor. Its solubility in water is so slight as to render this loss negligible, and it is not unlikely that the water employed is more or less saturated with N_2, thus rendering this error even smaller. The nitrogen is, therefore, a suitable basis for comparison of the gas entering and leaving.

Basis.—100 mols N_2.

RATIO TO 100 MOLS NITROGEN

Component	At Entrance	At Exit
SO_2	17.4/79.9 = 21.78	None
O_2	2.7/79.9 = 3.38	2.8/97.2 = 2.88

On first thought, it might be said that the ratio of oxygen to nitrogen should be the same at exit and entrance. There is, however, a noticeable decrease, which must be due to oxidation of SO_2, a reaction which does take place appreciably in dilute solution. This decrease of $3.38-2.88=0.50$ O_2 will oxidize twice that amount of SO_2, or 1.00 mol. Of the total SO_2 entering the tower, therefore, 1.00/21.78, or 4.59 per cent is oxidized to SO_3. Since only 96.3 per cent of the sulphur burnt enters the absorber as SO_2, the oxidation in the absorbers is 4.59 per cent of this, or 4.42 per cent, making a total of 8.12 per cent of all the sulphur burnt which goes to SO_3. All this enters the absorber, since the air is dry. Were it damp, the first 3.7 per cent would be condensed in the coolers as dilute H_2SO_4.

Basis.—One hour.

Lbs. crude sulphur	Lbs. S	Lbs. S in liquor as SO_2	Mols SO_2 in liquor	
680	0.994	(1.0-0.0812)	$\frac{1}{32.07}$	$\frac{5.90/2}{7.05}$ = 8.10 mols CaO+MgO per hr. for the combined SO_2 only

Basis.—100 lbs. lime.

$$\text{Mols of CaO} = \frac{82}{56} \ldots\ldots\ldots\ldots\ldots\ldots = 1.463$$

$$\text{Mols of MgO} = \frac{16}{40.3} \ldots\ldots\ldots\ldots\ldots\ldots = 0.397$$

$$\text{Mols of Total Oxides} \ldots\ldots\ldots\ldots\ldots\ldots = 1.860$$

Basis.—One hour.

	Mols	
Lime required = 8.10	$\frac{100}{1.86}$	= 435 lbs. lime per hr. for the combined SO_2 only

Lbs. crude sulphur	Lbs. S	Lbs. S as SO_3	Mols SO_3	
680	0.994	0.0812	$\frac{1}{32.07}$	= 1.71 mols oxides for SO_3

To get the various components in the liquor:

$$\text{Lime} = \frac{(8.10+1.71)\,(435)}{(8.10)} = 527 \text{ lbs. lime}$$

Lbs. crude sulphur	Lbs. S	Lbs. S as SO_2	
680	0.994	(1.0-0.0812)	$\frac{64.07}{32.07}$ = 1241 lbs. SO_2

Lbs. crude sulphur	Lbs. S	Lbs. S as SO_3	
680	0.994	0.0812	$\frac{80.07}{32.07}$ = 137 lbs. SO_3

Total weight of solids = 1905 lbs.

$$\text{Total weight liquor} = \frac{1241}{0.0705} = 17{,}600 \text{ lbs.}$$

(N.B. This is the answer to question 3.)

By difference, water in liquor = 15,700 lbs. To this must be added the water picked up by the gas, certainly small, but calculated as follows:

Cu. ft. gas per min.	Cu. ft. gas per hr.	Cu. ft. H_2O vapor	Cu. ft. at S.C.	Mols H_2O	
643	60	$\frac{22.7}{760}$	$\frac{492}{536}$	$\frac{1}{359}$	18.02 = 53.2 lbs. H_2O vaporized per hr.

The total water used is, therefore, 15,750 lbs. per hr.

CHAPTER II

FLUID FILMS

It has long been known,[1] though not generally appreciated, that when a gas or a liquid moves over a solid surface, or when a gas moves across a liquid surface, there exists a film of the moving substance upon the surface of the stationary one, of a character entirely different from that of the main body of the fluid. This fluid film forms a boundary or zone between the portion which is rapidly moving and that which is still, which acts towards the transportation of heat, vapor, and matter as though it were a separate material. Its properties are so controlling in many engineering processes that its presence and characteristics must be clearly recognized.

In a gaseous space of reasonable size, owing to the absence of appreciable frictional resistance, motion of the gas is extremely free and rapid. Any difference in pressure is rapidly and completely equalized. Differences in temperature also tend to disappear, due to mixing by convection. With liquids the same conditions exist, but owing to the increased resistance to motion, equalization is less perfect.

In contradistinction to this case of motion by convection within the fluid body, motion near the containing or limiting surface is of such a character that, compared to the main body of the fluid, this film may be considered stationary. Consider the case of continuous flow through a conduit. A plot of the motion of the gas as determined by the distance from the containing wall is shown in Fig. 8.[2] At the boundary wall itself there is no motion of the fluid. As one progresses from the wall, the velocity of motion of the fluid increases, but in the neighbor-

[1] The first mention of the water film was made by PECLET, "Traite de la Chaleur," Chap. VIII, p. 131, 1844. Since that time the presence and properties of such films have been verified by others, more particularly by Langmuir in 1912 (*Phys. Rev.* **34,** 421), who, working with gases, demonstrated the effect of velocity upon the thickness of the film, and upon heat transfer.

[2] Based on the data of STANTON, MARSHALL, and BRYANT, *Proc. Roy. Soc.*, Ser. A, **97** (1920), 413.

hood of the wall each element[1] of the fluid flows in a path parallel to the wall, having essentially no component of velocity at right angles to the wall. As one goes further from the wall, not only does velocity increase but also a point *FG* is finally reached at which the whole character of the motion changes. The elements of the fluid now begin to travel in forward-moving spirals. The net motion is still parallel to the surface, but the path of any one particle has a large average component at right angles to the surface. This complex motion obviously has a marked mixing effect on neighboring layers of the fluid and is described as turbulent.

Hence there exists on the boundary surface of a moving fluid a creeping film, traveling parallel to the surface at a speed considerably smaller than the average velocity of the fluid relative to the surface, but characterized preeminently by the fact that all bulk motion in this film is parallel to the surface and with no turbulent or mixing motion of the fluid elements. Consequently any motion through this film at right angles to the surface must be by the slow processes of diffusion. While all parts of this film other than that in immediate contact with the surface actually creep along the wall, it is easier to visualize the film as a stationary body of fluid and practically always allowable to do so. Where the motion of the main body of liquid past the surface is appreciable, this film is usually very thin.

When heat passes from a solid to a gas, for example, from a steam pipe to air, it can travel by conduction and diffusion, and to a very small amount by convection. A molecule of the gas strikes the steam pipe and is thrown off with greater velocity, *i.e.*, greater kinetic energy. If it strikes another molecule and imparts greater velocity to it, and this one to another, heat is passed out from the pipe by *conduction.* If this original hot molecule by its own motion passes out to the surrounding space, it carries heat by *diffusion.* If this molecule with many others is carried away from the surface of the pipe by a bodily movement of a quantity of gas, it carries heat by *convection.* Heat traverses this stationary film, however, by only conduction and diffusion

[1] Such an element is a very small body of the fluid but contains many molecules. Each molecule has its own irregular motion, but the whole group of molecules composing the fluid element moves as a unit, just as a raindrop falls vertically through quiet air, despite the irregular motion of the water molecules in the drop.

and is controlled by the laws governing these processes. Since in this case it is experimentally impossible to distinguish between true conduction and diffusion, the two are considered together and the term *conduction* applied to their combined effect. Of the total heat transported that lost by *radiation* is independent of the nature of the gas film (see pp. 160 to 171).

Vapor from liquids (or solids) can escape through this gas film only by diffusion. A molecule is thrown off from the surface

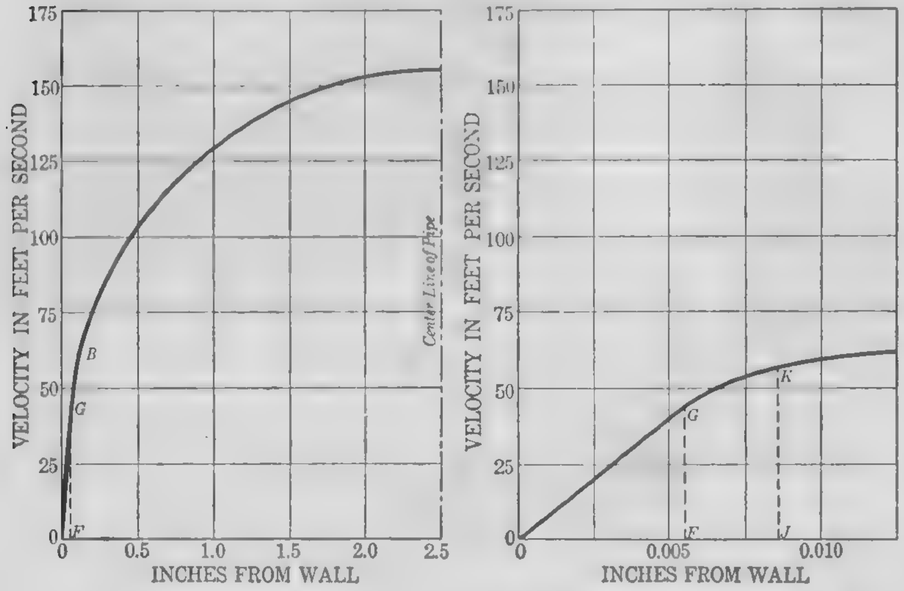


FIG. 8.—Velocity Distribution for Isothermal Flow in a Circular Pipe.

of the liquid and must work its way through the molecules of the gas forming the stationary film until it reaches the outside of the film and can be caught up and carried away by the convection currents there existing.

Where the main body of the fluid is flowing over the surface of the solid or liquid, the rolling or turbulent motion, existing at the surface of the boundary film, will wear away or rub off a portion of it, causing what amount to convection currents to strike more deeply into it. The thickness of the film is thereby decreased and any action resultant upon the presence of the film will be influenced accordingly.

This conception of a stationary film of gas or liquid is useful in the majority of operations in chemical engineering. Detailed applications of the idea will be made in the chapters dealing with the absorption of gases from gaseous mixtures by liquid absorbing agents, the removal of volatile from non-volatile material by passing through it a stream of air or other gas, the solution of solids by liquids, and those devoted to the transfer of heat in its many forms. Such phenomena are best explained by the assumption of the existence of the resistant film. Langmuir[1] has shown experimentally that such a film exists upon a hot silver plate to the depth of several millimeters (see p. 147). Under conditions where radiation was reduced to a minimum he slowly moved a delicate thermocouple from the surrounding air towards the plate. As long as the couple was more than a certain distance from the surface it remained practically constant, registering the temperature of the air rapidly moved about by convection currents. When it reached a definite small distance from the surface, the temperature began to rise progressively and quickly, finally reaching that attained when in contact with the plate. From the observed heat loss, corrected for the slight amount of radiation from the silver, the effective thickness of air film necessary to account for the loss was calculated as approximately 4 mm. The point at which the temperature starts to rise indicates the outer surface of the film, which in still air was from two to four mm. from the surface of the plate.

A theoretical consideration of the flow of gas through a capillary tube led Poiseuille to formulate a law which states that the volume of gas flowing through such a tube varies directly as the fourth power of the inside diameter of the tube. The derivation of this law is based upon the assumption, first that the main body of the gas assumes straight line flow rather than rolling or turbulent motion; second, that the friction is proportional to the relative slip of one layer of the gas on the next one to it; and third that there is no slip at the boundary wall. The fact that careful experiments with very narrow capillary tubes show this law to be quantitatively exact proves that the assumptions are correct, whence it follows that there is no flow in immediate contact with the wall.

[1] *Trans. Am. Electrochem. Soc.*, **23** (1913).

The mechanism of the diffusion of the vapor of a liquid from the liquid out into an inert gas (*e.g.*, air) with which it is in contact may be represented by the accompanying Fig. 9. Assume the line *OA* to represent a section of the surface of a volatile liquid in contact with air, the entire system being kept at constant temperature. The line *OB* represents the distance out into the air from the surface of the liquid and the line *HK* represents the outer surface of the stationary air film. In the direction *OA*, starting at the point *O* as an origin, the partial pressure of the liquid in question is plotted. The vapor pressure of the liquid at the temperature at which it exists is indicated by the point *C*. The partial pressure of the liquid in the main body of the air is, however, lower, as indicated by the point *D*. In the main body of the air the convection will keep the vapor so well mixed with the air that the partial pressure of the liquid will be practically constant, as indicated by the level of the horizontal line *DE*. Through the air film the vapor is not mixed by convection but passes by diffusion only. This diffusion will be produced by a partial pressure gradient, *CD*; but when the vapor has passed that film it will be mixed with the rest of the body of the air by convection, maintaining the constant partial pressure *DE* throughout the rest of the gaseous space.

If the air be inclosed and limited in amount, the continued diffusion of vapor into it will raise the partial pressure of the vapor until it reaches the value *FG*. This will have a corresponding effect on the pressure gradient through the stationary film, which is now represented by the line *CF*. This rise in partial pressure of vapor in the air will continue, the gradient through the surface film becoming less steep and diffusion therefore slower, until ultimately equilibrium is reached when throughout the gaseous space the partial pressure of the liquid has reached the value *C*.

Let the total pressure in the space be represented by the horizontal line *LM*. If not inclosed this will be constant at every point in the air whether near the liquid surface or not. Since at the surface of the liquid the vapor pressure of the liquid is equal to *OC*, the partial pressure of the air must be equal to *OL* minus *OC* or *ON*. Similarly, in the main body of the air the partial pressure of the air will be equal to *OL* minus *HD* or will be represented by the horizontal line *PQ*. The partial pressure of the

air in the stationary surface film will therefore be represented by the line *NP*. In other words, the partial pressure of air at the surface of the liquid is less than its partial pressure further out from the surface. Air does not, however, diffuse into the liquid, despite the existence of this pressure gradient, because of the impact against the air molecules of the vapor molecules driving out from the surface. This pressure gradient of air is maintained

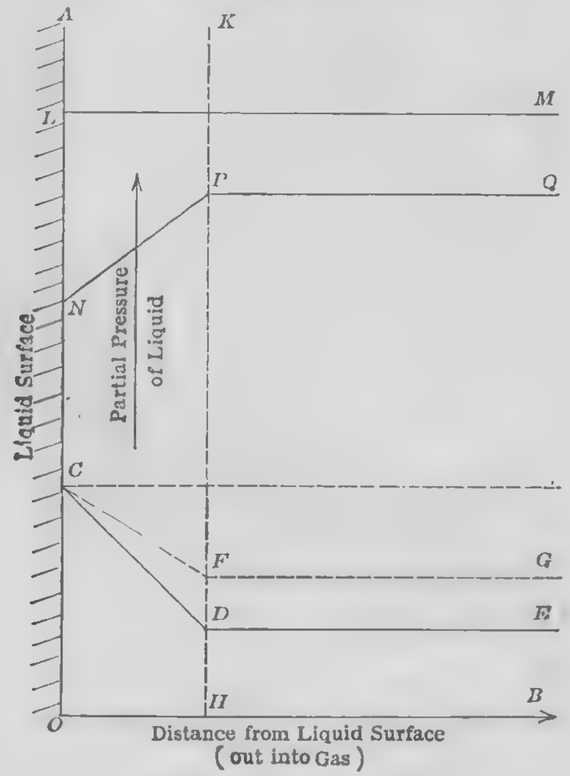


FIG. 9.—Diagram of Partial Pressures in a Fluid Film.

by a dynamic equilibrium controlled by the frictional resistance offered by the air film to the vapor molecules diffusing outward through it, and will be kept up until the liquid molecules have saturated the gas and the partial pressure of air on the liquid surface is therefore the same as in the main body of the gas.

The movement of matter through this stationary film requires diffusion. The diffusion velocities of gases and vapors are inversely proportional to the square roots of their molecular

weights. Small particles of solids or liquids suspended in the gas (*i.e.*, dust and fogs) may be considered as having indefinitely high molecular weights and therefore negligible diffusion velocities.[1] It is obvious that the gas film will effectively insulate such particles from the surface of liquid or solid in contact with the gas, so that interaction is difficult to secure.

Thus, whereas if one will bring either ammonia gas or dilute hydrochloric acid gas into contact with water both will be absorbed with great rapidity, on the other hand if one allows these two to interact in the gaseous state, forming a cloud of solid ammonium chloride particles, it is almost impossible to dissolve the latter. One can draw air containing such a cloud through a series of wash bottles highly effective for the absorption of gases, with almost no results.

This offers the explanation of the difficulty of absorbing sulphur trioxide made in the contact process. If one attempts to dissolve the trioxide in water or dilute sulphuric acid, the trioxide vapor first comes in contact not with the liquid but with the water vapor which has evaporated from the liquid into the gas. It reacts with this vapor, producing minute droplets of sulphuric acid in the form of a fog, and these droplets are effectively insulated from the absorbing liquid by the gas film. One must therefore use as an absorbent a liquid, the water-vapor pressure of which is negligible, *i.e.*, strong sulphuric acid. This is the reason why for absorption one must use acid between 97 and 98 per cent. If more dilute, the pressure of water vapor is sufficient to produce a fog, if more concentrated the partial pressure of SO_3 over it is great enough to prevent complete absorption. Fog formation is not necessarily dependent on chemical combination. Thus if air containing a high concentration of hydrochloric acid gas be brought into contact with water, the acid may combine with the water vapor and condense as a fog, which will likewise fail to be absorbed by the main body of the water.

These facts explain the difficulty of removal of tar from illuminating gas and producer gas, of cement dust and arsenic fume from stack gases, of carbon black formed by incomplete combustion of natural gas, and the like. (See pp. 329 to 334.)

[1] This is because, at constant temperature, the kinetic energy (proportional to the product of the molecular weight and the square of the molecular velocity) is the same for all gas particles.

CHAPTER III

FLOW OF FLUIDS

Introduction.—The movement of liquids and gases is of great importance because it is so often necessary to transport materials in one of these forms. Wherever a solid material in process is to be brought into solution eventually, it is generally much cheaper, and more convenient, to dissolve it at the start, thus transporting the solution, instead of conveying the solid itself.

The problems of fluid dynamics consist in first devising methods for measuring the quantity of fluid moving through a given system, and second, determining the power necessary to maintain the pressure essential to the required movement; in other words, to determine the motion of a fluid which results from a definite pressure difference.

Bernoulli's Theorem.—The solution of every problem in fluid dynamics is based on the law of conservation of energy, *i.e.*, on the equality of energy input to energy output in the whole or in any definite part of a system through which a fluid is flowing. The formula expressing this law is known as Bernoulli's theorem. It assumes the apparatus employed to be cut by two sections, chosen at any desired points across the path of motion, perpendicular to the direction of flow. It equates the total energy entering the apparatus per unit weight of the fluid at the first section to that leaving with the fluid at the second section, corrected, however, for any energy received or dissipated while between the two sections. As applied in hydraulics and in the hydromechanics of liquids in general, it is usual to equate merely the mechanical energy at inlet and outlet, since there is no transformation into heat energy, or vice versa, except that due to friction; where friction loss occurs it is subtracted from the energy input before equating to the energy output. On the other hand, whenever a compressible fluid, *i.e.*, gas or vapor, enters and leaves a section under differing pressures, the gas must have expanded within the section itself from the higher to the lower

pressure. In such an expansion a given portion of gas will do work upon the gas ahead of it, but in a system where the flow is continuous, it may be considered as doing the work upon itself or receiving the work from the gas behind it, thereby increasing its mechanical energy at the expense of its heat content (or that of its surroundings); hence, this expansion work must be added to the input of mechanical energy in the gas.

Bernoulli's theorem is used in two forms. The first represents an overall energy balance between the sections under consideration: the second represents a balance of mechanical energy only between those sections, corrected for mechanical energy received or dissipated between sections. The mathematical expression for the first form is

$$E_1+x_1+p_1v_1+u_1^2/2g+H+R=E_2+x_2+p_2v_2+u_2^2/2g, \quad (1)$$

and for the second

$$x_1+p_1v_1+u_1^2/2g+R+W=x_2+p_2v_2+u_2^2/2g+F. \quad (2)$$

The second form is the one most frequently used.

These equations assume one unit of weight (*i.e.*, in English units, one pound) of the moving fluid. E is the intrinsic energy of the fluid as it passes any specific section, x is the potential energy possessed by the fluid due to the action of gravity upon it, and is equal to the height of the fluid at the section above any arbitrarily assumed datum plane. This datum plane is usually chosen through the lowest point of the apparatus, in order to avoid negative values of the potential energy. The product, pv, is the mechanical work performed in forcing the fluid into or out of the section. The term $u^2/2g$ is the kinetic energy of the fluid due to its velocity. H is heat imparted to the fluid from the surroundings between the sections in question; it must of course be expressed in mechanical units, ft. lbs. per lb. R is any mechanical work done on the fluid by external means, such, for example, as by a pump. W is work done by the expansion of a fluid upon itself and is equal to $\int pdv$. F is friction loss, *i.e.*, mechanical energy converted into heat. Obviously, since the terms of the equations are additive, they must have the same dimensions and be expressed in the same units. Since the weight of fluid is one pound, the number of foot-pounds of energy is numerically equal to a distance expressed in feet, or a "head." Thus x is called

the potential head, pv the pressure head, and $u^2/2g$ the velocity head. One might speak of E and W as "heads," but this is not usually done. Using the concept of the energy terms as "heads," Eq. (2) may be written:

$$h_p'+h_s'+h_v'+R+W=h_p''+h_s''+h_v''+h_f,$$

where h_p, h_s and h_v are the respective potential, static (or pressure) and velocity heads at any two sections. This equality of the sum of the various terms at one section to a similar sum at a second section makes it clear that if any given head, for example, the velocity head, be made greater at the second section than at the first, there must be a corresponding decrease in one or more other terms at the second section.

Since the rate of flow is readily calculated if the velocity be known, many measuring instruments are designed to operate under conditions such that simple mathematical relations exist between a change in static head and the resultant change in velocity head. In order to have a clear understanding of the meaning of these terms, they will be defined.

Definitions.—*Fluid Head.*—Any kind of pressure exerted by a fluid (gas or liquid) at any point may be expressed in terms of the height of a column of fluid of equal density. The height of such a column is defined as the fluid head. Assume a vertical pipe of unit area of cross-section attached to the apparatus at the point where the fluid head is to be measured. The fluid will obviously rise in this pipe until the weight of the column of fluid exactly counterbalances the pressure above the atmosphere.[1] The height of such a column is called the fluid head, and it follows that this head multiplied by fluid density equals pressure per unit area in excess of atmospheric, *i.e.*, a ten-foot head of water, of density of 62.3 lbs. per cu. ft., is equivalent to a pressure (above atmospheric) of 623 lbs. per sq. ft. At a given point in a stationary fluid the pressure (or its equivalent, the fluid head) is the same in all directions. In a moving fluid this is no longer true, but the observed pressure varies as described below with the direction of the opening or orifice. Therefore, fluid head cannot be interpreted unless one knows the direction of motion of the fluid relative to the plane of the opening through which the head is transmitted for measurement.

[1] This assumes the fluid of constant density and immiscible with air.

In the case of a liquid, fluid head is often measured directly by the use of the liquid itself in a manometer (U-tube). In the case of a gas, it is almost always measured *indirectly* by the use of some liquid, such as water, in a U-tube. Equations are simplified by expressing the head in the terms of the fluid flowing. Hence, although in the case of gases the head is measured in terms of the height of that liquid actually used in the manometer, throughout the following it will be assumed that fluid head is expressed in terms of the fluid flowing; *e.g.*, if a gas exerts a head of 1 in. of water, it is assumed that this head will be converted into feet of gas by dividing by twelve (to convert the reading into feet) and then multiplying by the ratio of the density of water to the density of the gas at the point in question. Any fluid head can be expressed as a pressure per unit area and may, where practicable, be measured with an ordinary pressure gauge.

Pressure Head is defined as the fluid head exerted by a fluid upon a plane *parallel* to the direction of its motion (if any). Pressure head is usually measured, as indicated in the preceding paragraph, by attaching a manometer, one arm of which is open to the atmosphere, to the retaining wall which confines the fluid. If the fluid be in motion, the plane of the manometer opening must be parallel to the direction of flow, as otherwise the pressure exerted will be influenced by the tendency of the liquid to enter or leave the opening. In the case of a liquid, the pressure head is, therefore, the height (vertical distance) in feet from the point where the manometer is attached, to the free surface of the liquid in the manometer. If the liquid is at a pressure less than atmospheric, *i.e.*, if the pressure head is negative, a U-tube may be employed, one arm of which is open to the atmosphere. In this case the depression of the liquid level in the open arm is the negative pressure head. Since the free surface of the manometer is exposed to the atmosphere, the pressure head is referred to atmospheric pressure and is frequently called the *static head.*

In the case of gases, whether the pressure is positive or negative, an open U-tube containing a suitable liquid may be used. The difference in levels gives the head in feet of the liquid used which is converted into head of gas, by multiplying by the ratio of density of liquid to that of gas.

Velocity Head is defined as the fluid head exerted by a fluid upon a plane perpendicular to the direction of fluid motion *less* the pressure head at the same point.[1] If a small body be placed at a fixed point in a moving stream of fluid, this body deflects the small filament of moving fluid which would otherwise pass the point. The deflection of this filament involves first bringing it to rest. This requires the dissipation of its kinetic energy. It is found that this kinetic energy is quantitatively converted into additional fluid pressure. If, therefore, a small orifice or opening be inserted in a fluid stream, with the plane of the opening at *right angles* to the direction of motion of the fluid (the opening being so constructed as to interfere as little as possible with the motion of the stream as a whole, yet with no flow through the opening itself) there is exerted upon this opening a fluid pressure in excess of the static pressure by an amount equal to the velocity head. If such a small opening be connected with a manometer, the difference in reading between such a manometer and one connected with a static opening, the plane of which is parallel to the motion of fluid, will equal the velocity head.

Potential Head at any point is the vertical distance between the point and any arbitrarily chosen horizontal datum plane. (For convenience, to avoid negative values, the datum plane is usually taken through the lowest section.)

Gauges and Manometers.—*Pressure Gauges.*—For measuring static pressure of both gases and liquids when the pressure is considerably above or below atmospheric pressure the well known Bourdon type gauge is used. Such instruments should indicate a zero reading for atmospheric pressure, and usually the scale is graduated in terms of lbs. per sq. in. for pressures greater than atmospheric, and as inches of mercury for pressures less than atmospheric. It is advisable to calibrate such gauges, especially those that have been in service.

Differential Manometers.—As shown later, the rate of flow of fluids, as determined by orifices, Pitot tubes, Venturi meters, flow meters and closed conduits depends on a *difference* in head, expressed in feet of the *fluid flowing.* This difference in head (differential head) is often measured as the difference of two pressures, obtained by the use of a differential gauge (or manometer) such as the vertically placed U-shaped tube shown in Fig. 14, p.

[1] The fluid head exerted on the plane perpendicular to the direction of fluid motion is obviously the sum of the velocity head and the pressure head; this sum is sometimes referred to as the "impact head."

54. Consider two identical measuring instruments placed side by side, water flowing through one and air through the other, the linear velocities being the same, water being used in the manometers in both cases to measure the pressure drop. It will be shown later that the differential head is the same in both cases when *expressed in terms of feet of the fluid flowing*, and for the sake of definiteness this head will be taken as two feet. The reading (pressure drop) shown on the differential gauge in the first case (2 ft. of water) will be numerically equal to the drop in head produced by the flow (2 ft. of water) but in the second case the reading will be much smaller, due to the greater density of the water in the differential gauge compared to that of the gas flowing. If the density of air and water are taken as 0.075 and 62.3 lbs. per cu. ft. respectively, the reading (pressure drop) in the second case will be (2) (0.075)/(62.3) or 0.0024 ft. of water. In other words in the case of gases flowing at moderate velocities the reading is so small that precision is extremely difficult to obtain with a vertical U-tube using a liquid as the measuring medium, while with a liquid flowing at the same velocity much greater precision is easily obtained; conversely, the same precision is possible with much lower velocities for liquids than for gases.

In the case of *gases*, the differential head may be measured by the use of a glass U-tube partially filled with a suitable liquid. To avoid the accumulation of water or other liquid which may condense from the gas, the U-tube is placed *above* the point of attachment to the apparatus. In the case of *liquids*, the U-tube may be inverted; by partially filling the *upper* part with a gas, the liquid flowing may be used in the *lower* part of the tube. Where the U-tube is not inverted, it is convenient to employ in the lower part of the tube a liquid immiscible with the one flowing and of higher specific gravity. In the latter case, the desired difference in head equals the difference in levels of the measuring liquid in the two arms multiplied by the ratio $(y-s)/(s)$, where y and s are the specific gravities of the heavier and lighter liquids respectively.

Thus if an oil head is being measured by the use of mercury in a vertical U-tube, the oil filling the rest of the tube, the oil head will be (assuming $s=0.9$) the observed difference in mercury levels multiplied by $(13.6-0.9)/(0.9)$ or 14.1. Thus the reading is decreased due to the use of mercury, but the reduction is not nearly so great as when water is used to measure a gas head. Hence it follows that low liquid velocities may be measured with the same precision as high gas velocities, with the same type of manometer.

Multiplying Gauges.—Whenever the pressure difference to be measured is very small, the reading must be multiplied by some

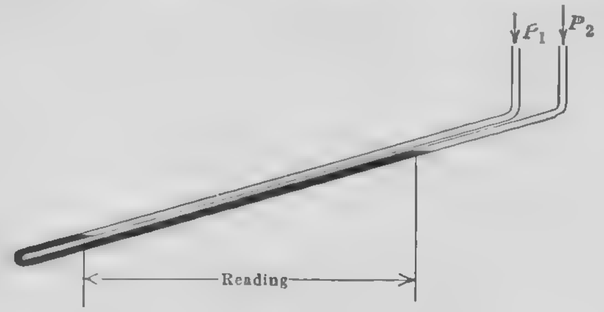


FIG. 10.—Inclined U-Tube.

mechanical device to make precision possible. Fig. 10 shows an inclined U-tube and Fig. 11 illustrates the draft gauge commonly used in the boiler room, both of which make the reading much greater than the difference in levels produced. The readings may easily be made ten times the difference in levels. Figure 12 shows

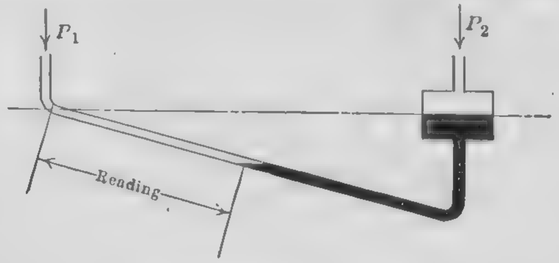


FIG. 11.—Draft Gauge.

a "multiplying gauge" in which the lower part of the vertical U-tube contains a liquid having a specific gravity only slightly greater than the one above it and not miscible with it. The diameter of the chambers A should be large compared to that of the U-tube B. The relation between the reading and the actual differential pressure is best determined by calibration, although it may be calculated from A, B and the gravities of the two liquids used. The pair of liquids chosen for use in a gauge of this type

should give a flat meniscus and neither of the liquids should tend to stick to the walls of the tube B. It is not safe to assume that the pair chosen will be absolutely insoluble in each other and hence the two liquids should be thoroughly agitated and the specific gravities of the two resulting saturated solutions accurately observed before placing them in the manometer. Although the effect of temperature on specific gravity is small, in this case it must not be overlooked as the difference in gravities is quite small. If the chambers A are quite large compared to the tube B the reading will then equal $1/(y-s)$ times the inches of water

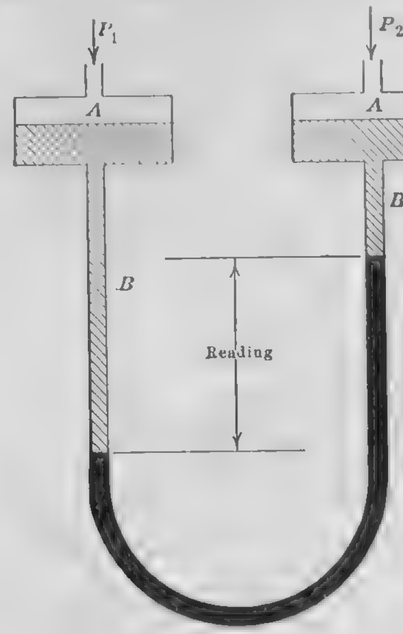


FIG. 12.—Multiplying Gauge.

pressure difference applied, y and s being the specific gravities of the heavier and lighter of the two solutions, respectively. Assuming a suitable pair of saturated solutions having gravities of 0.8315 and 0.7905, the reading will be 1/(0.0410) or 24.4 times the inches of water pressure difference applied. If the reading in this case were 4 in. the actual pressure difference applied would equal 0.164 in. water.

Piezometer Ring.—As stated above, the static pressure is measured by a gauge or a manometer attached to a small opening in the walls of the conduit, the plane of the opening being *parallel* to the direction of flow of the fluid. Thus in order to measure

the static pressure in a steam or water main, a Bourdon type pressure gauge is connected to a small opening tapped into the wall of the main. However, in many cases it is necessary to determine with great precision small differences in static pressure. In such cases a number of static openings should be made at the section in question, the openings being connected to a manifold from which the average static pressure is obtained. Such a device is called a Piezometer ring (see Fig. 13) and is constructed as follows: Four or more very small holes a are drilled through the walls of the conduit at equal intervals around the circumference of the section

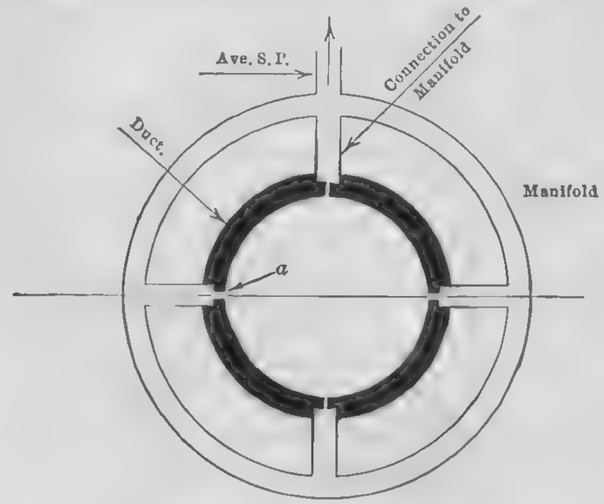


FIG. 13.—Piezometer Ring.

in question, and after a short distance are enlarged to take a pipe of a convenient size, say $\frac{1}{4}$ in. Connecting pipes are screwed in and joined to a manifold encircling the conduit, and the average static pressure is measured by a gauge or a manometer attached to the manifold. The holes a are made very small ($\frac{1}{64}$ in.) for two reasons: first, it is easier to make the planes of the openings parallel to the walls of the conduit in the case of small openings than with larger ones, and second, if the pressure on one static opening is different from that on another (as may often be the case) the smallness of the opening a will retard the flow of fluid through the ring from one opening to another, and hence the desired *balancing* in the connecting ring of the pressures on the various openings is more nearly attained. It is clear from the above description that the Piezometer ring is an automatic

averaging device, intended to reduce error in observation by taking the mean value of a number of independent values.

METHODS FOR MEASURING THE RATE OF FLOW OF GASES, VAPORS AND LIQUIDS; RELATION BETWEEN PRESSURE DROP AND RATE OF FLOW

As already stated, the most important problem of fluid dynamics is the determination of the quantitative relations between fluid velocity and pressure drop. This is necessary, first, to determine the power consumption required for a given flow, and second to determine the rate of flow from direct measurement of pressure drop. For the latter purpose one should employ types of apparatus in which the mathematical relations between velocity of flow and pressure drop are simple and universally valid. Because of their simplicity the most important measuring devices will be treated first, and in the following order:

I. Standard Orifice.
II. Venturi Meter.
III. Pitot Tube.
IV. Other Devices.
  1. Gasometers and Receivers.
  2. Addition or Removal of Energy, or Foreign Material.
  3. Gas and Water Meters (Mechanical Types).
  4. Anemometer.
  5. "Flow-Meters."
V. Friction of Flow through Conduits.
  A. Circular Cross-sections.
  B. Sections other than Circular.
VI. Contraction and Enlargement Losses.

Under each case the equations necessary for calculating the relation between the pressure drop and the rate of flow are given, with illustrative problems for various gases and liquids. Following this discussion is a Summary of Equations and Nomenclature Table. The derivation of the equations will be found on pp. 102 to 117, the equation numbers being consistent throughout. The term "*upstream*" is used to designate the *first* section of the apparatus passed by the fluid, while the term "*downstream*" refers to the last section that the fluid passes, and these sections are designated by the subscripts "1" and "2" respectively. The term u, unless otherwise defined, represents the *average* velocity of the fluid as feet per second, namely the cubic feet of fluid passing per second divided by the area of the opening in square feet, regardless of whether or not the fluid fills the opening.

Limitations to Equations.—The equations given throughout the following discussion of measuring devices are valid for all pressure drops for the flow of *liquids*, and they apply equally well to the flow of *gases* and *vapors* when the pressure drop does not exceed ten per cent [1] of the downstream *absolute* pressure. Equations are given in the Summary of Equations for the cases where the pressure drop is greater than this.

I. STANDARD ORIFICE

One of the common methods of determining rate of flow of gases, vapors and liquids is to measure the pressure drop caused by the insertion of a *suddenly* restricted opening or orifice of known size into the line (see Fig. 14). In this way a definite measured portion of the static head above the orifice is transformed into velocity head in the restricted section. Since the observed decrease in static pressure is caused by the increase in fluid velocity, the flow is calculated from the following equation:

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where u_1 is the upstream *average* velocity and u_2 is the *average* velocity through the orifice, both expressed in *feet per second*, c is a coefficient of discharge, g is the acceleration due to gravity (32.2 *ft. per second per second*) and Δh is the observed decrease in static pressure expressed in *feet* of the fluid flowing of the downstream density.

As indicated diagrammatically in Fig. 14, in the important special case in which the diameters of the chambers are five times that of the orifice, the contraction of the stream issuing from the orifice is greatest at a distance equal to four-tenths the inside pipe diameter downstream from the plane of the orifice, and the fluid

[1] The pressure drop is rarely as great as this for the flow of gases and vapors, as usually such a large drop would be uneconomical. The most important exception to this rule is found in the transportation of compressed gases through pipe lines.

stream has not started to contract at a point eight-tenths inside pipe diameter upstream. Hence the pressure connections should be made at these specified distances [1] from the plane of the orifice. This is important as the values of the coefficient of discharge quoted below were determined under these conditions. If there were no friction due to the passage of the fluid through the constriction and if the constricted opening did not cause the stream lines to converge, the coefficient of discharge c in the above equation would be unity. With the standard types of opening used in practice the actual flow is less than the theo-

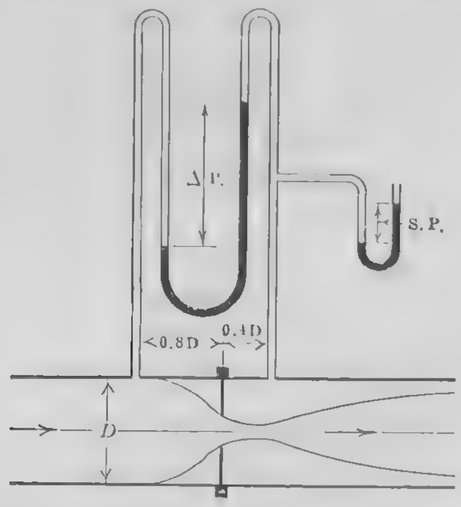


FIG. 14.—Orifice and Differential Gauge.

retical value based on the assumption of frictionless flow and no contraction of the stream, and hence the value of c is less than unity. The coefficient of discharge is practically constant at 0.61 for the "sharp-edged" orifice (Figs. 15*A* and 15*B*), provided the diameter of the orifice is large, compared to the thickness of the plate, and 0.98 for the rounded orifice (Fig. 15*C*), when used with suitable orifice chambers (see below) and when the orifice is concentric with the pipe. The coefficient for the "standard short tube" (Fig. 15*D*) may vary widely with conditions and its use is not recommended.

The so-called "sharp-edged orifice in a thin plate," Fig. 15*A*, is best made by drilling a hole in a metal plate varying in thickness from $\frac{1}{16}$ in. to $\frac{3}{16}$ in. If a thicker plate is required to withstand

[1] See DAVIS and JORDAN, *Bull.* **109**, Univ. of Ill. Eng. Expt. Sta. (1918).

the pressure, the edge of the hole is beveled to a sharp-edged circular hole of the desired size, the sharp edge being pointed *upstream* as in Fig. 15*B*, but it is difficult to make this latter type exactly circular.[1] A glance at Fig. 15*C* shows that the rounded orifice is also difficult to construct. Since the sharp edge orifice is most easily and cheaply made it is the one commonly used.[2]

In constructing a standard orifice, chambers having diameters five times that of the orifice should be inserted above and below the orifice.[3] This is recommended for three reasons. First, the

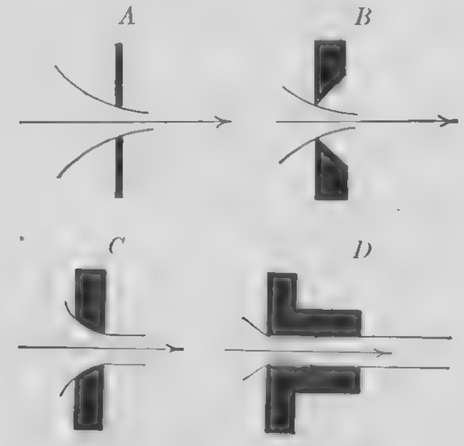


FIG. 15.—Orifices and Short Tube.
A. Sharp-edged Orifice in Thin Plate.
B. Sharp-edged Orifice in Thick Plate.
C. Rounded Orifice in Thick Plate.
D. Standard Short Tube.

eddy currents above and below the orifice are less violent, and hence the static pressure may be determined more accurately. Second, the coefficient of discharge c remains nearly constant at 0.61 for the "sharp-edged orifice in a thin plate," whereas this would not have been the case with smaller chambers. Third, the equation is simplified as the square of the velocity of approach, u_1^2 becomes negligible as compared with the square of the velocity

[1] A better construction is to reinforce the back of the plate in *A*.

[2] In chemical work it possesses the extremely important advantage that c is practically independent of the viscosity of the fluid, even up to several hundred times the viscosity of water.

[3] The justification of recommending this limitation will be appreciated if the reader will study the complicated relationships found when inadequate chambers are used. See JUDD, "Experiments on Water Flow through Pipe Orifices," *Trans. A. S. M. E.*, **38**, 331 (1916), and DAVIS and JORDAN, *loc. cit.*

in the orifice, u_2^2. With such chambers the above equation becomes

$$u_2 = c\sqrt{2g(\Delta h)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Where the orifice is designed to avoid a high friction loss, Δh will be small; hence to obtain precision a Piezometer ring must be employed (see p. 50). If these precautions be observed, a standard orifice may be inserted at any point in the line and the actual discharge will correspond within a few per cent to that calculated though for very accurate work it must be calibrated.

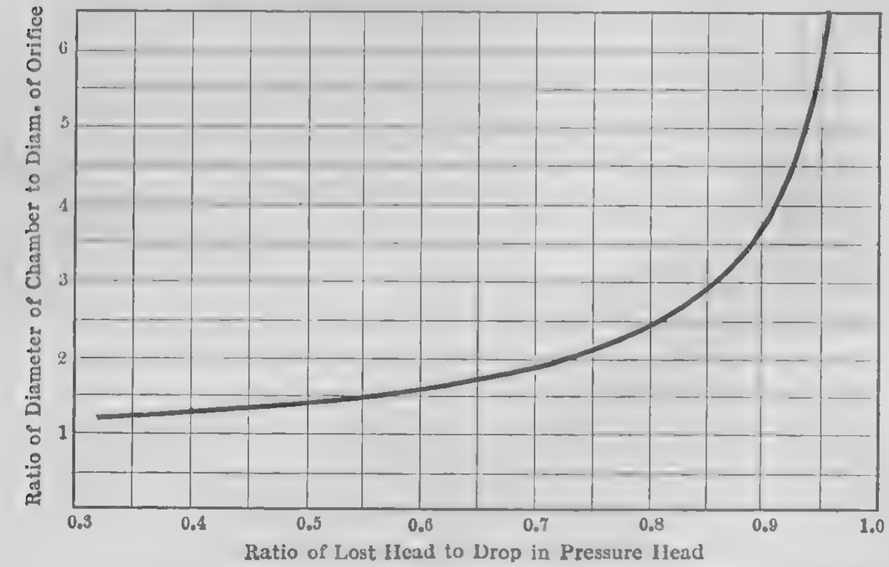


FIG 16.—Plot Showing How Head Lost in Sharp-edged Orifices Varies with Ratio of Diameters of Chamber and Orifice.

Although the cost of the apparatus is low the disadvantage of this method is that a *permanent* loss of nearly the whole of the observed drop in static pressure results because of the *sudden* velocity changes; hence the pressure drop should be the smallest possible consistent with the precision desired in measuring the flow. This lost energy may become so large that it may be more economical to employ another type of apparatus (Venturi meter) which, although it has a higher initial cost, gives approximately one-tenth the *permanent* friction loss for an equal reading of the pressure drop.

Fig. 16[1] shows how the ratio of the lost head to the drop in

[1] DAVIS and JORDAN, Univ. of Ill. Eng. Expt. Sta., *Bull.* **109** (1918).

pressure head caused by a sharp-edged orifice varies with the size of the orifice chambers expressed as the ratio of the diameter of the chambers to that of the pipe.[1] For chambers having diameters five times that of the orifice, the lost head is 93 per cent of the reading.

Illustration 1 (Gas).—Hydrogen gas at 70° F. is flowing through an 8-in. i. d. galvanized iron pipe which has been gradually enlarged to 20 in. to form the chambers for an orifice drilled to 4 in. in a $\frac{1}{16}$-in. galvanized iron plate, the hole being centered with the center line of the pipe. Sixteen inches upstream from the orifice and 8 in. downstream Piezometer rings have been installed on the chambers; a vertical U-tube partially filled with water and connected to these Piezometer rings, shows a difference in levels of 1.21 in. A second U-tube partially filled with water, one arm of which is open to the atmosphere, is attached to the downstream Piezometer ring and shows 4 in. of water pressure above atmospheric pressure. Calculate the flow of *dry* hydrogen in lbs. per hour and the power cost of operating the orifice per 24-hr. day (*a*) assuming the gas to be dry, and (*b*) assuming it saturated with water vapor. The barometer is 29.2 in. of mercury, and the vapor pressure of water at 70° F. is 0.74 in. of mercury. Combined efficiency of fan and motor is 50 per cent, and power costs 3 cents per k.w.h.

(*a*) **Solution (Gas Dry).**—Since the diameter of chambers is five times that of the orifice, Eq. (18) is used, and since the orifice is sharp-edged, $c = 0.61$.

$$u_2 = 0.61\sqrt{2g(\Delta h)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The downstream pressure is $29.2 + \frac{4}{13.6} = 29.5$ in. of mercury, so the downstream density of the gas is

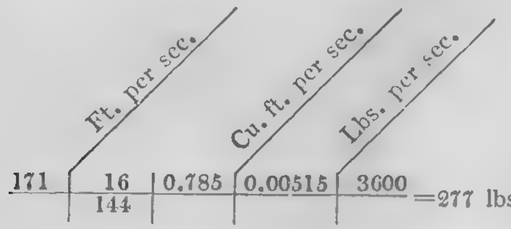
	At S.C.	At 70° F., 29.9 in.	
2.02 / 359	192 / 530	29.5 / 29.9	= 0.00515 lbs. per cu. ft. at 70° F. and 29.5 in. mercury absolute pressure

$$(\Delta h) = \frac{(1.21)\,(62.3)}{(12)\,(0.00515)} = 1220 = \text{differential head calculated as feet of gas.}$$

$$u_2 = 0.61\sqrt{(2)\,(32.2)\,(1220)} = 171 \text{ ft. per sec. average velocity}$$

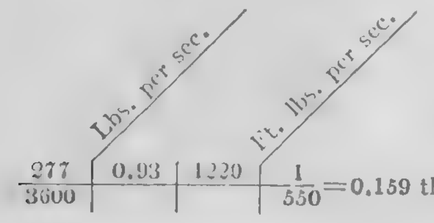
[1] This phenomenon is due to a partial building up of the pressure below the point of maximum contraction, Fig. 14, p. 54.

through the 4 in. orifice. Hence

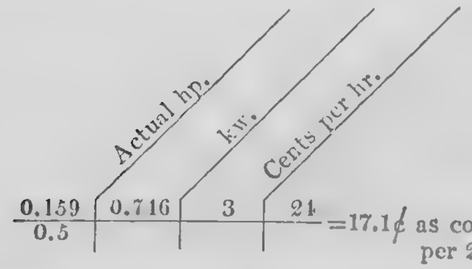


$=277$ lbs. dry H_2 per hr.

Assuming 93 per cent of the differential head (1220 ft. of gas) to be lost, as indicated in Fig. 16, the power equivalent is



$=0.159$ theo. hp. or



$=17.1¢$ as cost of lost power per 24 hr. day

(*b*) **Solution (Gas Wet).**—The average molecular weight =

$$\frac{(2.02)\,(29.5-0.7)}{(29.5)}+\frac{(18)\,(0.74)}{(29.5)}=1.97+0.45=2.42.$$

The calculations for part (*b*) could be made similar to those in part (*a*), allowing for the higher density in part (*b*). Instead of doing this, part (*b*) has been calculated from part (*a*) by the use of ratios, as shown below.

From part (*a*) it is evident that the lbs. gas flowing per hour is determined by the product of the density and the inverse square root of the density, giving as a net result the square root of the density. Hence the lbs. *wet* gas per hour =

$$(277)\sqrt{\frac{2.42}{2.02}}=303.$$

Since in every 2.42 lbs. of wet gas there are 1.97 lbs. dry hydrogen, the *dry* hydrogen present in the mixture =

$$\frac{(303)\,(1.97)}{(2.42)}=247 \text{ lbs.}$$

per hour which is about 11 per cent less than in part (*a*).

The daily power cost for part (*a*) was 17.1 cts. and for part (*b*) it will be greater by the ratio of $\sqrt{2.42/2.02}$, to allow for the greater weight of the wet gas, and by 2.02/2.42 to allow for the lesser gas head, with the net result that the power cost $(17.1)\sqrt{2.02/2.42}=15.6$ cts., or about 9 per cent less than in part (*a*). However, per 1000 lbs. of dry hydrogen delivered, the cost when wet is 2.3 per cent greater than when dry.

NOTE.—The accuracy of the calculations is probably not better than 2 per cent.

Illustration 2 (Water).—Water is flowing through a 6-in. i. d. cast-iron pipe at an average velocity of 5 ft. per sec. under a gauge pressure of 50 lbs. per sq. in. It is proposed to install a sharp-edged circular orifice and the pressure drop through the orifice is not to exceed 5 lbs. per sq. in. What should be the dia. of the orifice and how much power will be lost due to its use?

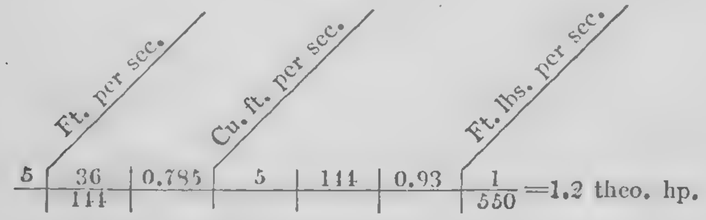
Solution.—Since the coefficient of discharge may be assumed as 0.61 only when suitable chambers are used, such chambers will be provided, and hence Eq. (18) applies.

Since the water is practically incompressible it is unnecessary to know the static pressure of the water; $\Delta h=(5)\,(144)/62.3=11.6$ ft. of water. Calling the orifice dia. in inches D_2, $u_2=(u_1)\,(6)\,(6)/(D_2)^2=180/(D_2)^2$. By Eq. (18),

$$u_2=(0.61)\sqrt{(64.4\,(11.6)}=\frac{180}{D_2{}^2},$$

whence $D_2=3.29$ in.

Assuming that 93 per cent of the specified pressure drop of 5 lbs. per sq. in. is lost, the lost power is



$=1.2$ theo. hp.

Illustration 3 (Oil).—A 3-in. i. d. sharp-edged orifice has been installed in a 6.07-in. i. d. steel pipe carrying a mineral oil of sp. gr. 0.900, the orifice being provided with 16-in. chambers. A vertical U-tube containing mercury and oil shows 4 in. difference in mercury levels. Calculate the flow of oil as bbls. per hour and the power lost due to the orifice.

(NOTE.—One oil bbl. = 42 U. S. gals; sp. gr. mercury = 13.6.)

Solution.—By Eq. (18),

$$u_2 = c\sqrt{(2g)\ (\Delta h)}$$

$$u_2 = (0.61)\sqrt{\frac{(64.4)\ (4)\ (13.6-0.9)}{(12)\ (0.9)}}.$$

Whence $u_2 = 10.6$ ft. per sec. through the 3-in. orifice. Hence the flow =

	Ft. per hr.		Cu. ft. per hr.		Gals. per hr.	
10.6	3600	9 / 11	0.785	7.48	1 / 12	= 344 bbls. per hr.

By Fig. 16, 94 per cent of the observed drop will be lost. Hence the theoretical power consumption equals

	Ft. per sec.		Cu. ft. per sec.		Lbs. per sec.		Ft. lbs. per sec.	
10.6	9 / 144	0.785	62.3	0.9	1 / 12	(13.6-0.9) / 0.9	0.94 / 550	= 0.235 theo.hp.

II. VENTURI METER

The Venturi meter operates on the same principle as the standard orifice, and measures the decrease in static pressure due to an increase in the velocity of a fluid stream caused by a known reduction in the cross-section of path. The striking difference in the form of the standard orifice (Fig. 14) and Venturi meter (Fig. 17) lies in the fact that the changes in cross-section are sudden in the former and *gradual* in the latter.

The equation is,

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{2g(\Delta h)}, \quad . \ . \ . \ . \ . \quad (28)$$

where u_1 and u_2 are the *average* fluid velocities as feet per second at the upstream and throat sections respectively, g is the acceleration of gravity, (Δh) is the observed decrease in static head expressed as feet of fluid flowing of the density at the throat section, and c is

the coefficient of discharge (see Standard Orifice above). Since the cross-section of the pipe is gradually reduced to that at the throat, the convergence of the stream lines is not nearly so marked in the Venturi meter as in the sharp-edged orifice, and hence c is larger for the former than for the latter. In the standard orifice, the section is *suddenly* enlarged from that of the orifice to that of the downstream chamber or pipe with the result that the greater proportion of the velocity head (created in the orifice at the expense of the static pressure in the upstream chamber) is not reconverted to static pressure in the downstream chamber, but is lost by impact and internal friction. The Venturi meter possesses a great advantage over the standard orifice by reason

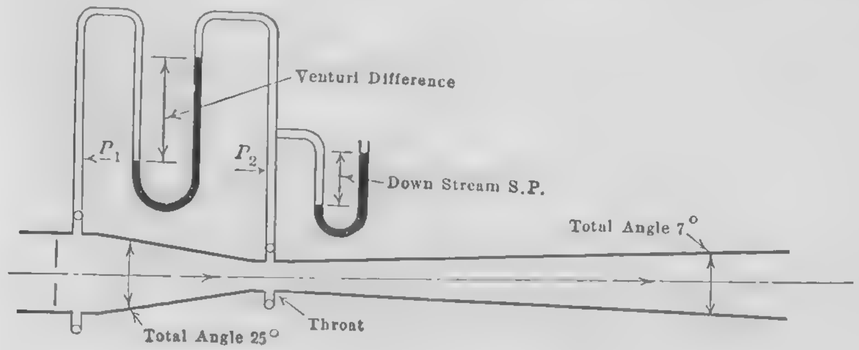


FIG. 17.—Venturi Meter.

of the fact that the permanent reduction in the static pressure is very small because the velocity head (created in the throat at the expense of the original static pressure) is largely reconverted to a static pressure by the *gradual* enlargement of the section to its original size.

The construction of the Venturi meter is shown in Fig. 17. The throat diameter is usually from $\frac{1}{2}$ to $\frac{1}{4}$ the upstream diameter, and the throat length should not exceed one throat diameter. The *total* angle of divergence of the two tapered sides should not exceed 7° on the downstream side nor 25° on the upstream side. In order to minimize the friction loss and to insure a high and constant coefficient of discharge the throat should be lined with bronze and very accurately bored to size and finished. Under these conditions the permanent loss in static pressure is only $\frac{1}{16}$ to $\frac{1}{8}$ of the Venturi reading, and the coefficient of dis-

charge c will be from 0.97 to 0.99. For very accurate work the instrument should be calibrated.

In inserting the Piezometer rings, care should be taken that the connections to the static openings do not project into the sections; otherwise serious errors in the readings will result. Since it is necessary to make the total angle of divergence small in order to obtain a value of c of nearly unity, the length of the Venturi meter is great relative to the diameter of the line in which it is inserted. Tests [1] for gas on a compact Venturi meter made of galvanized sheet iron, having total angles of divergence of 60° and 15° on the upstream and downstream sides respectively gave a coefficient of discharge of 0.85 to 0.88, when the rate of flow was determined by a standard sharp-edged orifice placed in series with this Venturi meter. The Venturi meter is used in the illuminating gas industry and elsewhere with great success. It is unsatisfactory for viscous liquids.

Illustration 4 (Gas).—A properly made Venturi meter having a throat diameter of 2 ft. is inserted in a 4-ft. main carrying illuminating gas at 70° F. The gas has a density of 0.6 referred to air of the same temperature and pressure, the barometer is 29.25 in. of mercury, and the reading on a (10 horizontal to 1 vertical) inclined differential U-tube [2] containing gasoline (sp. gr. = 0.685) is 0.90 and the static pressure at the throat is 2 in. of water above atmospheric pressure. Calculate (a) the rate of flow as cu. ft. per hr., and (b) the hp. loss due to the presence of the instrument.

Solution.—(a) The absolute pressure of gas at the throat corresponds to 2 in. of water above the barometric pressure of 29.25 in. of mercury, namely

$$29.25+\frac{2}{13.6}=29.4 \text{ in. mercury.}$$

The gas density at the throat is

$$\frac{(29)\ (492)\ (29.4)\ (0.6)}{(359)\ (530)\ (29.9)}=0.0443 \text{ lb. per cu. ft.}$$

The differential head as feet of gas (Δh) is

Reading	In. of gasoline	Ft. of gasoline	Ft. of water	
0.90	$\frac{1}{10}$	$\frac{1}{12}$	0.685	$\frac{62.3}{0.0413}$ = 7.23 ft. of illuminating gas

[1] G. H. Porter, Undergraduate Thesis, M.I.T., 1920.

[2] The average molecular weight of air is 29.0, see p. 5.

By Eq. (28)

$$\sqrt{u_2^2-u_1^2}=0.98\sqrt{(2g)\ (\Delta h)}.$$

Neglecting changes in pressure $u_1=u_2/4$ and this becomes

$$u_2^2-\frac{u_2^2}{16}=(0.98)^2\ (64.4)\ (7.23),$$

whence $u_2=21.8$ ft. per sec. through the 2-ft. throat, and hence (21.8)(3600)(3.14) = 247,000 cu. ft. per hr. flowing at 70° F.

(b) The gas flowing is

$$(21.8)\ (3.14)\ (0.0443)=3.04 \text{ lbs. per sec.,}$$

so the power consumed by the instrument, assuming one-eighth of the reading to be lost, is

$$\frac{(7.23)\ (3.04)}{(8)\ (550)}=0.0050 \text{ theo. hp.}$$

III. PITOT TUBE

The pressure on the end b of an open tube (Fig. 18) pointing directly against the gas stream (*i.e.*, on the impact opening) is the

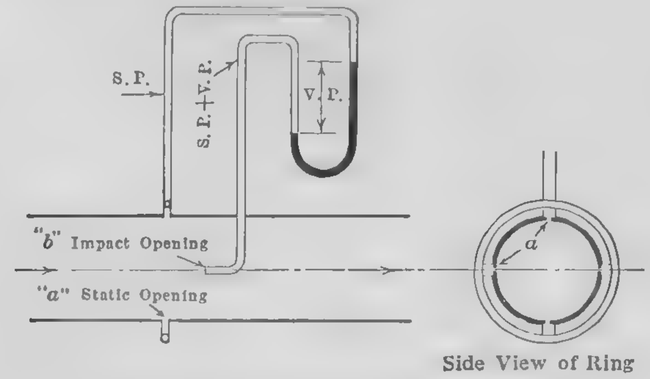


FIG. 18.—Open Tube and Piezometer Ring.

sum of the velocity and static pressures, while that on openings a whose plane is in that of the gas stream (namely, on the static openings) is the static pressure only. The difference between the two is the velocity pressure at the impact opening.

The instrument most frequently used for measuring this difference is known as the "Pitot Tube."

From the definition of velocity head it is obvious that the

equation connecting the *actual* velocity (u_{act}) in ft. per sec. *at the point where the tube is inserted is given by*

$$u_{act} = \sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where Δh is the differential reading due to the velocity head expressed as ft. of the fluid flowing. Applications of this equation will be given below.

One form of tube consists of two concentric tubes containing a 90° bend as shown in Fig. 19, the impact opening *b* being at the open end of the inner tube, and one or more static openings *a* in the outer tube. Thus the static openings are inserted along with the

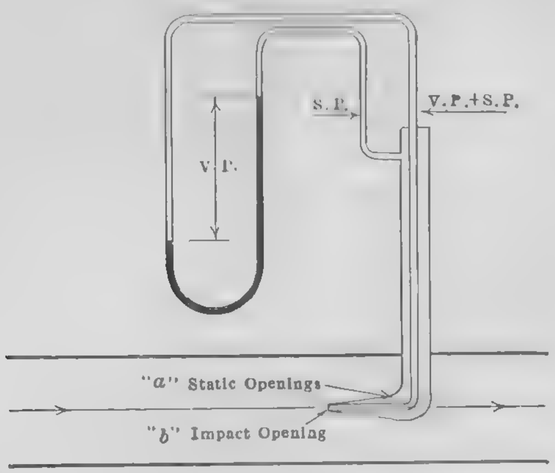


FIG. 19.—Pitot Tube.

impact opening, and exploration work is facilitated. The difficulty with this arrangement lies in the fact that the very insertion of the Pitot tube itself deflects the fluid stream, thus obviously interfering with the accurate determination of static pressure. Fig. 19 illustrates an attempt to avoid this evil by the use of four static openings with the idea that if the pressure is too high on one of them it will be too low on some of the others and thus a true average static pressure will be obtained. Certain manufacturers offer Pitot tubes in which this counter-balancing of errors on the static orifices is not satisfactorily accomplished, but in such cases the makers usually furnish a coefficient for their particular type of instrument. The calibration of such instruments is essential.

The velocity of a fluid flowing in any conduit always varies at different points in a section taken at right angles to the direction of flow. This variation is extremely erratic in bends, tees, valves, and at points near the entrance or exit to any straight section of pipe. Experiments have shown that this variable behavior is minimized if the observations be taken at a section not less than 50 diameters from any " point of disturbance " (bend, valve, etc.). The distance should be increased where possible.

Pitot tubes are used for exploration purposes to measure the flow in apparatus already built, as the instrument can be inserted through a small hole in the conduit, which can later be closed. In certain cases, for example, where a fan is placed in the middle of a short air duct drawing from and delivering into an open space, the gas flow is so erratic that it is necessary to determine the velocity at many points in a cross-section. For this purpose the Pitot tube is of great value since no other method is available.

As shown above, the static pressure in a conduit is best measured by equalization of the pressure upon a number of small openings in the walls of the conduit, *i.e.*, by the use of a Piezometer ring, p. 51. Hence greater accuracy can be obtained if the combination of " open tube and Piezometer ring " be substituted for the tube shown in Fig. 19. This modification consists in installing a Piezometer ring on the conduit, and in placing a small open tube pointing directly against the gas stream one inch downstream. This arrangement is shown in Fig. 18. The diameter of the tube carrying the impact opening *b* should be small relative to that of the conduit, so that the presence of the impact opening will not materially increase the gas velocity in the conduit.

The disadvantage of the Pitot tube when used for gases is the fact that, owing to their low density, the readings at moderate velocities are very small, and liable to error. Thus, the differential reading where air at 70° F. and atmospheric pressure is flowing at a velocity of 10 ft. per sec. is only 0.0224 in. of water, and when flowing at 30 ft. per sec. is 0.202 in. of water. Where such low readings are encountered[1] the differential pressures are

[1] This difficulty does not arise where velocity and pressure are high as in mains for superheated steam. Very satisfactory steam meters of this type are available using mercury as liquid. Both indicating and recording instruments are built.

best measured by an inclined gauge or by a multiplying gauge. When water flows at these same velocities, owing to its greater density, the readings are $62.3/0.075=832$ times the above. *It is obvious that there is no appreciable power loss due to the presence of a Pitot tube in a fluid stream.*

In the absence of the disturbing effects of bends, etc., it has been found that the ratio of the average velocity to the maximum velocity at the center line of the pipe increases with values of the "modulus" $\frac{du_{max}\rho}{\mu}$, as shown in Fig. 20. For values of the *absolute* viscosity (μ) of fluids, see pp. 77 to 85. The ratio of the

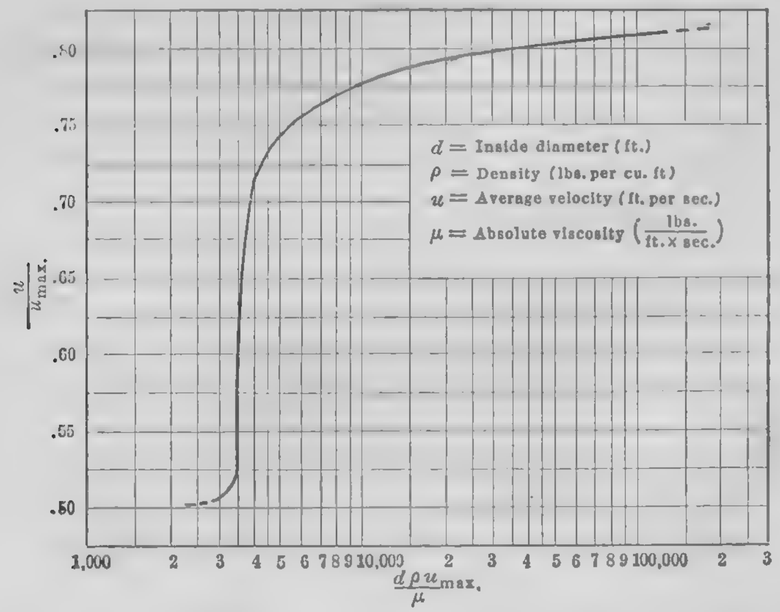


FIG. 20.—Ratio of Mean Velocity to Maximum Velocity in Circular Pipes.
From Nat. Phys. Lab., 11 (1914)

average velocity to the maximum velocity is only 0.50 when "straight line" motion (see p. 73) exists, *i.e.*, at values of $du_{max}\rho/\mu$ of *about* 2500 or less. For larger values of the modulus the flow is "turbulent" (see p. 74), and since the degree of turbulence or mixing of the stream increases with increasing values of the modulus, the ratio u/u_{max} becomes larger. In the past engineers have assumed the velocity ratio as about 0.8, which was a good approximation due to the facts that the curve is quite

flat in the turbulent region and that most of the conditions met happened to be turbulent.

In the case of gases straight line motion is seldom found in practice; where it does occur in gas flow the velocity would probably be so low that the differential reading on the Pitot tube would be so small as to make precision impossible with the types of differential gauges commonly used. However, in the case of viscous oils, straight line motion may occur, even at high velocities, especially in small pipes. In any case, it is well to employ Fig. 20 to determine the probable value of u/u_{max}, as is done in the illustrative problems following. For precision, the value of this velocity ratio should be determined experimentally. This is of especial importance in the neighborhood of the critical value of the modulus where the velocity ratio varies widely with a small change in the modulus.

One of the interesting modifications [1] of the Pitot tube is the so-called "Pitot-Venturi Tube" which is designed to give a larger reading than a Pitot tube.

Illustration 5 (Gas).—A commercial Pitot tube similar to the one shown in Fig. 19 is inserted at the center line of a horizontal 12-in. i. d. galvanized iron pipe carrying dry air at 70° F. at a static pressure of 2 in. of water above atmospheric pressure, and the horizontal deflection on a U-tube (inclined 10 in. horizontal to 1 in. vertical and connected to the impact and static openings) shows 2 in. of water. The Pitot tube is at a distance of 50 pipe diameters (50 ft.) from any obstruction in the pipe. Calculate (*a*) the *actual* velocity of air as ft. per sec. at the point where the reading is taken, (*b*) the *average* velocity as ft. per sec. at this cross-section, (*c*) the rate of flow as cu. ft. per min., and (*d*) as lbs. per hr. Barometer is 29.75 in. of mercury.

Solution.—The density of the gas at the point of reading is

$$\frac{(29)\ (492)\left(29.75+\frac{2}{13.6}\right)}{(359)\ (530)\ (29.9)}=0.0750 \text{ lb. per cu. ft.}$$

The horizontal deflection on the inclined U-tube is 2 in. but due to the 10 to 1 inclination the actual difference in levels is only 0.2 in. of water. Since the density of the liquid used in the manometer (water) is 62.3 lbs. per cu. ft., the height of air column equivalent to the 0.2 in. water column is

$$\frac{(0.2)\ (62.3)}{(12)\ (0.075)}=13.85 \text{ ft. of air.}$$

By Eq. (35), $u_{act}=\sqrt{2g(\Delta h)}=\sqrt{(64.4)\ (13.85)}=29.9$ ft. per sec. at the point where the reading was taken, namely, the center line of the pipe.

[1] FALES, *J. Am. Soc. Heating Ventilating Eng.*, **28**, 1–10 (Jan., 1922).

From Fig. 23 it is seen that the *absolute* viscosity of air at 21° C. is about 0.000180 c. g. s. units, which must be multiplied by 0.0672 (see p. 85) to convert it into English units. The value of the modulus for this case is then

$$\frac{du_{max}\,\rho}{\mu} = \frac{(1)\ (29.9)\ (0.075)}{(0.000180)\ (0.0672)} = 18{,}500 \text{ and}$$

from Fig. 20, $u = 0.79u_{max}$. Hence,

$$u = (0.79)\ (29.9) = 23.7 \text{ ft. per sec. (F. P. S.)}$$

Since the cross-sectional area is 0.785 sq. ft. the rate of flow is

$$(23.7)\ (60)\ (0.785) = 1120 \text{ cu. ft. per min. (C. F. P. M.)}$$

or

$$(1120)\ (60)\ (0.075) = 5050 \text{ lbs. per hr.}$$

Illustration 6 (Water).—A 6-in. i. d. cast-iron water main is carrying water at a temperature of 20° C. and a pressure of 50 lbs. gauge, and the reading on a vertical U-tube containing mercury (sp. gr. 13.6) and water is 1 in., the U-tube being connected to a Pitot tube placed at the center line of the pipe at a distance of 25 ft. from any obstruction in the pipe. Calculate the rate of flow in cubic feet of water per second and as U. S. gals. per min.

Solution.—The effective sp. gr. of the measuring liquids is $13.6-1=12.6$ so that 1 in. differential reading corresponds to a velocity head of

$$\frac{(1)\ (12.6)}{(12)\ (1)} = 1.05 \text{ ft. of water.}$$

By Eq. (35)

$$u_{act} = u_{max} = \sqrt{2g\Delta h} = \sqrt{(64.4)\ (1.05)} = 8.23 \text{ F. P. S.}$$

Since the absolute viscosity of water in English units is 0.000672 (p. 85),

$$\frac{du_{max}\,\rho}{\mu} = \frac{(0.5)\ (8.23)\ (62.3)}{(0.000672)} = 382{,}000,$$

$u = 0.817u_{max}$ (Fig. 20). Then u will be 6.73 ft./sec. and the discharge will be

$$\frac{(6.73)\ (3.14)}{16} = 1.32 \text{ cu. ft. per sec.,}$$

or

$$(1.32)\ (60)\ (7.48) = 593 \text{ U. S. gals. per min.}$$

Illustration 7 (Oil).—A Pitot tube is inserted into a 4.07-in. i. d. steel pipe carrying a mineral oil at 100° F. The Pitot tube is at the center line at a distance of 25 ft. from any obstruction, and shows a reading of 0.80 in. on a vertical U-tube containing both mercury and the oil. Assuming that the viscosity of the oil at 100° F. (relative to water at 68° F.) is (*a*) 50 and (*b*) 300, calculate the flow as bbls. per hr.

(NOTE.—One oil-bbl. = 42 U. S. gals.; sp. gr. of oil at 100° F. = 0.900).

Solution.—The actual velocity at the center line of the pipe as given by Eq. (35) is

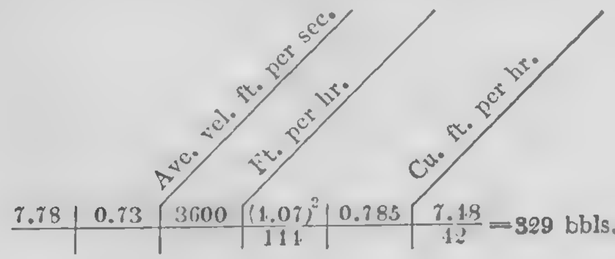
$$u_{max} = \sqrt{(2g)\ (\Delta h)} = \sqrt{\frac{(64.4)\ (0.8)\ (13.6-0.9)}{(12)\ (0.9)}} = 7.78 \text{ F. P. S.}$$

Before the rate of flow as bbls. per hr. can be calculated it is necessary to find the value of u/u_{max}, as the volume flowing per hour is determined by the product of the cross-section and the *average* velocity over that cross-section.

Since the absolute viscosity of water is 0.000672 in English units, p. 85,

$$\frac{du_{max}\,\rho}{\mu} = \frac{(4.07)\ (7.78)\ (62.3)\ (0.9)}{(12)\ (0.000672)\ (50)} = 4420$$

and from Fig. 20, $u = 0.73u_{max}$.[1] Hence the rate of flow is,



For case (*b*) modulus is one-sixth as large as for case (*a*), and by Fig. 20, $u = 0.50u_{max}$, whence the discharge equals 225 barrels per hr. Although the Pitot tube gave exactly the same reading in both cases, the flow in the second case, because of the higher viscosity of the oil, was only 68.5 per cent of that in the first case.

IV. *A.* OTHER DEVICES (GASES)

(1) Gasometers and Receivers.—A gasometer is an inverted vessel, usually a cylindrical metal one, placed concentrically inside another vessel containing a liquid, generally water. When the gasometer is empty the inner vessel is full of liquid, and as the gas is fed in through a pipe projecting up through the bottom of the outer tank the inner vessel rises by an amount proportional to the quantity of gas admitted. Gasometers are used widely in the illuminating gas industry.

The change in the amount of gas in a constant volume storage tank may be measured by observing the change in the pressure or

[1] As previously indicated, the value of u/u_{max} is uncertain in the neighborhood of values of the modulus of 2500, and in such cases exploration is very desirable.

weight. The constant volume receiver is employed for high pressures, as in the determination of the rate of discharge of air from a compressor. The measurement of gases by weight is usually unsatisfactory because the weight of the tank is so great relative to that of the gas, that results obtained by difference may have little accuracy unless the gas be under very high pressure.

(2) Addition (or Removal) of Energy, or Foreign Material.—The amount of gas flowing past a given section may be determined by injecting a measured amount of something into the gas and measuring the concentration of it in the final product after perfect *distribution has been attained.* Knowing the amount of the thing admixed and the concentration before and after the addition, it is possible to calculate the amount of gas to which it is added. For example, the rate of chlorine evolution from an electrolytic cell may be determined by feeding air at a known constant rate into the gas as it leaves the cell, and by analyzing the gas before and after the air has been added. Again, the amount of air passing through a humidifier or drier may be calculated from the known evaporation and the humidities of the entering and exit air. Frequently, it is convenient to add or remove heat in the form of electrical energy at a known rate and to measure the change in temperature. The Thomas Gas Flow Meter, which is based on this principle, consists of an enlargement of the pipe carrying the gas, in which is inserted first a thermometer of the electrical resistance type, then electrical resistance wire uniformly distributed across the whole section of the pipe in which a known amount of electrical energy is transformed into heat (this energy being measured by a wattmeter) and finally on the downstream side, another thermometer similar to the first. The Thomas meter automatically controls the electrical input so as to maintain a constant small temperature rise between the thermometers and measures the electrical input necessary to maintain this rise. This electrical input is proportional to the amount of gas passing the section, since the specific heat of any gas is constant over the temperature range involved. However, the operation must be automatic in order to get satisfactory results, because under ordinary conditions the temperature fluctuations of the entering gas are very large compared with the rise in the temperature of the gas in the meter. Hence an attempt to measure the quantity of gas by admitting a constant amount of *energy* and

determining the temperature rise is highly unsatisfactory. Thomas meters are usually of the "integrating" type, *i.e.*, the instantaneous rate is integrated with respect to time, giving the total flow over a period of time.

(3) Mechanical Gas Meters.—The amount of gas flowing past a section may be measured by the insertion of a mechanical meter, of which various recording types are obtainable. Such meters should be carefully standardized, generally against a gasometer or other apparatus. They are mechanical devices which are expensive and liable to get out of order. Where large quantities of gas are to be measured constantly, they are employed, as in the illuminating gas industry. Such meters have the advantage that they record the total flow over a period of time; the rate may be determined by taking readings at desired intervals.

(4) Anemometers.—The anemometer is a small windmill, the friction of which is reduced to a minimum and the rate of rotation of which should therefore be proportional to the velocity of the gas current in which it is placed. It consists of a light vane wheel fixed on a shaft, the rotation of which is recorded by a counting mechanism. Such instruments must be standardized with the greatest care at velocities as nearly as possible equal to those to be measured, and even when so treated are liable to wide variations in behavior; while very convenient, the instrument is unsatisfactory on this account. However, they are useful for exploration work, and unless very sensitive multiplying gauges are used with the Pitot tube, at gas velocities below 5 ft. per second give greater accuracy. Anemometers are seldom made for gas velocities higher than 40 or 50 ft. per second. Obviously the usual types of anemometer cannot be used in corrosive atmospheres or where the gas is excessively hot.

(5) Flow-Meters.—The term "flow-meter" is sometimes used to designate any restricted opening or tube through which the rate of flow has been determined by calibration. For example, a 2-in. pipe may be bushed down to $\frac{1}{2}$ in. and then enlarged to 2 in.; the pressure drop through this opening is a measure of the rate of flow, but this relation should be determined by calibration.

For laboratory work, where the rate of flow of gas is small, capillary tubes of 1 to 12 in. in length are used to produce the pressure drop, which is recorded by means of a U-tube connected by tees to chambers at both ends of the capillary. Usually these

are calibrated[1] over the desired range by measuring the volume of water displaced (gasometer method). Flow-meters for liquids similar to those described for gases are cheaply made both for laboratory and plant use.

IV. *B.* OTHER DEVICES (LIQUIDS)

When liquids are to be measured, the gasometer is replaced by a measuring tank, or by a weighing tank.

The principle of measuring the change in the concentration of a foreign material in water may be applied to continuous evaporation. The rates of feed and discharge may be calculated from the rate of condensation and the analysis of the entering and exit solutions; or the rate of evaporation may be calculated from the rate of feed and entering and exit concentrations. The rate of liquid flow through a cooler may be calculated from the specific heat of the liquor, the entering and exit temperatures of liquor, and the heat picked up by the cooling water. In both cases, correction should be made for heat interchange with the surroundings.

There are various types of water meters, as described in the handbooks of mechanical or hydraulic engineering.

[1] A. F. BENTON, *J. Ind. Eng. Chem.*, Vol. 11, No. 7, pp. 623 to 629 (July, 1919), states that for laboratory flow-meters in *which straight line flow exists* the reading on the differential gauge (in mm. water) is equal to $1.263\frac{RL}{d^4}+67.9\frac{R^2}{d^4}$, where R=rate of *air* flow in liters at 25° C. and normal barometer per minute, L=length of capillary tube in mm., and d=internal diameter of capillary in mm. This equation was found to hold for air. The first term in the right-hand side of the equation gives the pressure drop due to the viscous flow in the capillary itself, while the term following allows for the entrance and exit losses. Where the capillary is sufficiently long to make the latter term negligible compared to the former, it is suggested that the calibration for gases other than air can be predicted approximately by multiplying the coefficient 1.263 by the ratio of the viscosity of the gas in question at 25° C. to that for air at the same temperature. *For accurate work, flow meters should be calibrated.*

V. FLOW OF FLUIDS THROUGH CONDUITS

Mechanism of Flow.—This discussion will be limited to "steady flow" *i.e.*, flow at a constant fluid velocity, or what is the same thing, under "constant head." The movement of the fluid is caused by a difference in total head between the two points under consideration. For example, a liquid will flow from point (*a*) at atmospheric pressure through a conduit to another point (*b*) at atmospheric pressure providing the second is at a lower level than the first; in such a case the flow would be due entirely to difference in potential head. A fluid will flow from a point of high pressure at (*c*) through a horizontal pipe to a point of lower pressure at (*d*), in which case the flow is caused entirely by difference in pressure head. Obviously the flow can be caused by a *net* difference in the sum of the pressure and potential head. Two types of motion are possible, as shown below.

A—CIRCULAR CROSS-SECTIONS (PIPES)

Straight Line Flow.—Every fluid (gases, vapors, water and oils) flows in straight line motion at low velocities. In this type

FIG. 21.—Velocity Distribution in Circular Pipes.
A. Straight Line (Viscous) Flow.
B. Turbulent (Eddy) Motion.
Abs. = actual *net* velocity at a given point.
Ord. = distance from center line of pipe.

of motion every particle of fluid flows in a direction parallel to the walls of the pipe, and there are no "transverse" or mixing currents. There is no motion whatever at the wall itself but as the center line of the pipe is approached the velocity increases. (See Fig. 21*A*.) As shown on pp. 65 and 66, if the velocity at the center line be determined at a sufficient distance (50 pipe diameters) from any obstruction, such as a bend, valve, etc., the *average* velocity over the entire cross-section is one-half the maximum value which is found at the center line of the pipe. The equation of flow is given by Poiseuille's law which may be derived from the definition

of absolute viscosity by the aid of the calculus and which has been experimentally confirmed for diameters ranging from those of capillary tubes up to 12-in. pipe:

$$\Delta p = \frac{32\mu Lu}{gd^2}, \quad \ldots \ldots \quad (56)$$

where Δp = pressure drop as *lbs. per sq. ft.*

L = length of straight pipe in *feet* plus " equivalent length " due to bends, etc. (See p. 100 for data.)

u = average velocity of fluid as *feet per second* (cubic feet per second divided by cross-sectional area in sq. ft.)

d = inside diameter of pipe in *feet.*

μ = absolute viscosity in English units (*second poundals per square foot = lbs. per sec. per ft.*).

The term *absolute viscosity* [1] which appears in the above equation is a measure of the internal fluid friction, and is most simply described as the coefficient μ in Poiseuille's law. Each fluid has a definite viscosity at a given temperature, and the absolute viscosity of fluids varies with temperature.

Turbulent Motion.—In the case of every fluid as the velocity is increased, some point is reached where the type of motion *suddenly* changes from straight line motion to a second type of motion known as turbulent motion, which is characterized by the presence of innumerable eddy currents in the stream. (See Fig. 21B.) In this type of motion there is relatively little or no motion of the fluid at the pipe wall. Experimentally it is found that the ratio of the average velocity for the whole cross-section to the maximum value at the center line is higher than in straight line flow. If the velocity at the center line be determined at a sufficient distance (50 pipe diameters) from any obstruction, the

[1] Assume a large flat trough containing a stationary mass of liquid. If a very large plate having the same density as the fluid be pulled through the mass of liquid in a horizontal plane, it will be found that adjacent layers will start to move, owing to cohesive action between the particles. The particles nearest the moving plane will move more rapidly than those further removed, and hence there is set up a shearing action between the particles in adjacent planes. When the velocity of a mass of particles of liquid in a plane of unit area and unit distance away from and parallel to the moving plate differs from that of the plate by unity, the force per unit area on the moving plate will be numerically equal to the absolute viscosity.

ratio u/u_{max} is approximately 0.8. (See Fig. 20.) The equation of flow for turbulent motion is given by Fanning's equation:

$$\Delta p = \frac{f\rho Lu^2}{2gm} = \frac{4f\rho Lu^2}{2gd}, \quad \ldots \ldots \quad (38)$$

where m = hydraulic radius in *feet* = area of cross-section in square feet divided by wetted perimeter in feet = $d/4$ for circular pipes.

ρ = density of fluid as *lbs. per cu. ft.* = $62.3s$, where s is the sp. gr. relative to water.

f = friction factor (no units) which varies with the " modulus " $\frac{du\rho}{\mu}$, as shown later.

The factor of four in the numerator in Eq. (38) is omitted in a few text books, thus making the value of the friction factor four times those given here, but the majority of engineers use the Fanning equation as given above, Eq. (38).

Critical Velocity.—The velocity at which the type of motion changes from straight line to turbulent flow is called the *critical velocity*, and in practice may differ widely as shown below. If for any definite pipe diameter, viscosity, and density a plot (see Fig. 22) be made with Δp as ordinates and u as abscissae, Eq. (56) gives a straight line starting at the origin while Eq. (38) gives a curve concave upwards which crosses the straight line at the critical velocity. It is an experimentally determined fact that for velocities less than the critical the flow will follow Eq. (56) and for velocities greater than the critical the flow will correspond to Eq. (38).[1] This is equivalent to stating that the pressure drop at any given velocity will be the higher of the two values shown in Fig. 22; at a given pressure drop the velocity will be the smaller of the two values shown in Fig. 22. *Thus the less favorable of the two possible conditions is always obtained.*

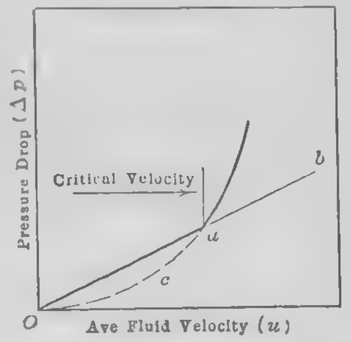


FIG. 22.—Critical Velocity.

Since at the critical velocity u_c the pressure drop is equal for

[1] See footnote on p. 76.

both types of motion, Eqs. (56) and (38) may be equated in order to determine the critical velocity. As shown later the friction factor f in Eq. (38) varies with the velocity of the fluid and other conditions, and calling its value at the critical velocity f_c,

$$\Delta p_c = \frac{32\mu L u_c}{gd^2} = \frac{2f_c \rho L u_c^2}{gd}, \text{ whence}$$

$$u_c = \frac{16\mu}{f_c \rho d}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

It will be shown on p. 87 that the friction factor in cast-iron or steel pipes at the critical velocity is the same for all fluids, namely, $f_c = 0.0170$, hence Eq. (59) becomes *for all fluids*

$$u_c = \frac{912\mu}{\rho d}.^{1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59a)$$

This equation states that the critical velocity is large for large absolute viscosity, small fluid density and small inside pipe diameter. Of these three factors, two (μ and ρ) vary with the nature of the fluid and the ratio (μ/ρ) is sometimes called the *kinematic viscosity*. In calculations involving liquids, it is convenient to replace μ, d, and ρ by the terms z, D and s, where z is the viscosity of the liquid at the temperature in question relative to water at 68° F., D is the pipe diameter in inches, and s is the sp. gr. of the liquid. By substituting $\mu = 0.000672z$, $d = D/12$ and $\rho = 62.3s$ in Eq. (59a) the latter becomes, for *steel* pipe,

$$u_c = \frac{0.122z}{Ds} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59b)$$

[1] When a fluid is flowing in straight line motion and the velocity is *gradually increased*, it is possible to obtain velocities higher than the critical and yet the flow will be in straight line motion. This corresponds to the unstable condition indicated by the line *ab* in Fig. 22. In such a case the actual pressure drop would be given by Poiseuille's law, Eq. (56), but if the critical velocity be calculated by Eq. (59) the pressure drop would be calculated by Eq. (38) for turbulent motion, thus giving a calculated pressure drop higher than the actual one. If the fluid be flowing in turbulent motion and the velocity be *gradually decreased* it might be possible to obtain unstable turbulent motion, as shown by the line *ac* in Fig. 22. If Eq. (59) be used to calculate the critical velocity, it would be assumed that the unstable flow is on the line *oa* for straight line flow in which case the calculated pressure drop would again be higher than the actual one. Thus it is seen that it is wise in all cases to regard the point at which the two curves cross in Fig. 22 as a definite point, as calculated from Eq. (59), for if unstable flow of either type develop the calculated pressure drop will be on the safe side, namely, higher than the actual.

which is more convenient for liquids, and applies equally well to gases.

The following table shows the critical velocities calculated from Eq. (59b) for flow through a *standard* 2 in. pipe. Since the *actual* inside diameter of such a pipe is 2.07 in., (see p. 101), for this case Eq. (59b) becomes

$$u_c = \frac{0.122z}{2.07s} = 0.0589\frac{z}{s}$$

CALCULATED CRITICAL VELOCITIES IN STANDARD 2-IN. PIPE

Fluid	Temp., °F.	Abs. press., atm.	Specific gravity, $s = \rho/62.3$	Relative viscosity, centipoises	Critical velocity, ft./sec.
Hydrogen	70	1	0.0000834	0.0088	6.2
Air	70	1	0.0012	0.0184	0.904
Air	70	10	0.0012	0.0184	0.0904
Steam	212	1	0.00060	0.0120	1.18
Steam	357	10	0.00524	0.0144	0.162
Water	68	Any	1.0	1.0	0.059
Refined oil	68	Any	0.90	10.0	0.65
California crude oil	68	Any	0.963	3,450	211

It will be seen that the critical velocities of *air* and *water* are so low compared to those used in commercial pipe lines that straight line flow will not be found in practice for these fluids, unless the pipe diameter is quite small. In the case of viscous oils, however, the critical velocities may be much higher than the velocities used in commercial lines. Since the density of such liquids varies but little, the critical velocity is determined mainly by the ratio of the viscosity to the inside diameter of the pipe.

As will appear on p. 87, the relation between pressure drop and rate of flow of fluid through a pipe line for both types of motion depends on the viscosity of the fluid. Viscosity data may be obtained by the use of various apparatus, and for a given fluid varies with temperature. The data may be expressed in several systems of units; hence these phases will be discussed before taking up the problems requiring the use of the equation of flow.

Viscosity of Gases.—The absolute viscosity of a gas may be determined by applying a definite pressure difference at the two

ends of a capillary tube of known length and diameter and observing the rate of flow, μ being calculated from Poiseuille's law. Such measurements are difficult to make, because it is difficult to obtain a capillary tube of uniform diameter. This difficulty, however, can be avoided by measuring relative viscosity (see p. 80). Since the viscosity varies with temperature, the determination should be carried out at a constant temperature. Fig. 23 shows the viscosity of certain gases at various temperatures. The viscosity of gases is approximately proportional to a positive

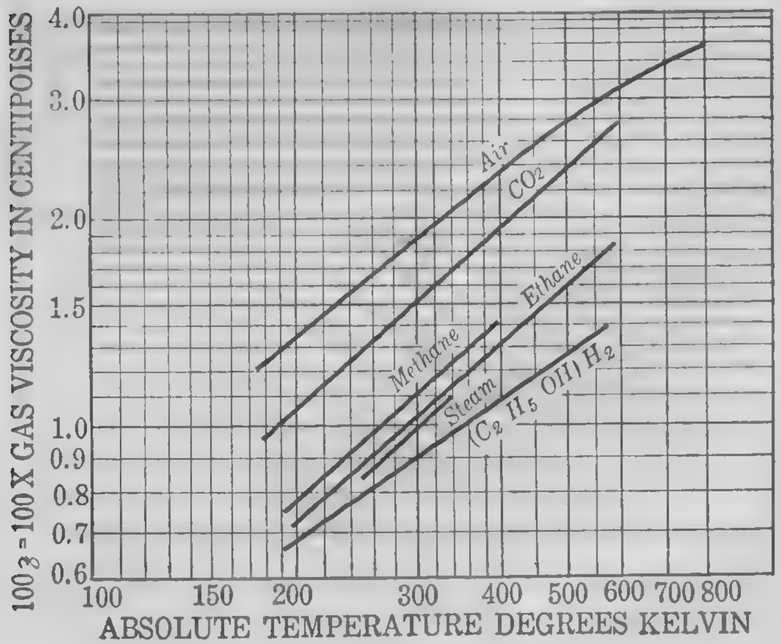


FIG. 23.*—Viscosity of Gases.

* Data from various sources in the literature.

power function of absolute temperature. In plotting such data on logarithmic paper it is found to fall on very flat curves in most cases, the average slopes varying from 0.5 to 1.[1] Additional data

[1] According to kinetic theory, the viscosity of gases should be independent of pressure and directly *proportional* to the square root of the absolute temperature. Experimental data show that the viscosity of carbon dioxide gas is practically independent of pressures from $\frac{1}{10}$ to 1 atmospheres, and even at forty atmospheres pressure it has increased by only about 18 per cent. (JEANS, "Dynamical Theory of Gases," Camb. Univ. Press, 1904.) However, the exponent of the absolute temperature is nearer unity than the value of 0.5 called for by the kinetic theory.

may be found in suitable physical-chemical tables, and it is customary to tabulate the absolute viscosity in c. g. s. units. The method of converting these to other units is given on p. 85.

Viscosity of Liquids.—The absolute viscosity of liquids may be determined by the use of a capillary tube, as discussed below, by the use of the MacMichael viscosimeter, and in other ways.

In commercial work, the viscosity of a liquid is generally determined by measuring the time of efflux of a definite volume through a short tube in an apparatus called a *viscosimeter*. Thus a liquid with a viscosity of 80 Saybolt is one requiring 80 seconds to discharge a volume just sufficient to fill the chamber of the Saybolt viscosimeter through the orifice of that instrument under the changing though definite head which that instrument gives. The pressure drop through the tube itself is dependent upon the absolute viscosity of the liquid, but the entrance and exit losses are practically independent of the absolute viscosity; hence the absolute viscosity is not directly proportional to the time of efflux.

The relation between the time of efflux (θ) in *seconds* and the viscosity varies for different makes of viscosimeters, and sometimes even for the various instruments supplied by a given manufacturer. Such instruments are calibrated against liquids of known viscosity. For the *new* standard Saybolt, the relation, is as follows:

$$\frac{z}{s} = 0.220(\theta) - \frac{180}{\theta}, \quad \ldots\ldots\ldots \quad (65)$$

where z is the viscosity at any definite temperature *relative to water at 68° F.* and s is the specific gravity at the temperature in question. Thus an oil of 100 Saybolt seconds and sp. gr. of 0.9 at 150° F. would have at this temperature a relative viscosity of $(20.2)(0.9) = 18.2$. This empirical equation is satisfactory where the flow through the Saybolt nozzle is viscous. If liquids of low viscosity are used this will not be the case and hence the equation is inapplicable. For example, it would indicate a negative viscosity for a time of discharge less than 28.6 sec.

As indicated above, the absolute viscosity of a liquid may be determined by observing the time of efflux of the fluid through a

capillary tube. Lang [1] has shown that viscosity may be determined quickly and with reasonable accuracy by the use of a capillary tube, the lower end of which dips into a large dish containing the liquid being tested. The tube is adjusted so the liquid rises by capillarity to a definite, fixed mark. A second mark is chosen somewhat above this. Suction is then applied to the top of the capillary tube and a column of the liquid is drawn up above a third mark near the top of the tube. The column is allowed to fall and the time (θ_x) required for the liquid to fall from the third to the second mark is observed. From a similar observation on the time (θ_s) for a standard liquid whose absolute viscosity is known, the viscosity of the liquid x is calculated from the following equation, derived from Poiseuille's law:

$$\frac{\mu_x}{\mu_s} = \frac{\theta_x(\rho_x)}{\theta_s(\rho_s)}, \quad \ldots\ldots\ldots \quad (66)$$

where ρ is the liquid density.

Inasmuch as the viscosity of most liquids changes quite rapidly with the temperature, for accurate work the capillary should be jacketed. This approximate method should not be used where the viscosity of the standard liquid and that of the liquid in question are widely different.

In the case of *liquids*, the viscosity always *decreases* as the temperature rises. Where data at a few temperatures only are available, it is often necessary to interpolate and sometimes to extrapolate on the curve of viscosity versus temperature, but there is no satisfactory simple equation which can be used to predict the viscosity for all liquids. As shown in Fig. 24 the curvature is great at some temperatures and little at others. It is well known that interpolation and extrapolation are most reliable when the data can be made to approximate a straight line relationship. Thus by plotting the reciprocal of the viscosity against the temperature, or the logarithm of viscosity versus the reciprocal of the absolute temperature, or the logarithm of viscosity versus the logarithm of the absolute temperature, or the logarithm of viscosity versus the temperature, the curvature is greatly reduced, but none of these methods gives a straight line relationship in all cases. Although the method [2] illustrated by Fig. 25 has not yet

[1] Undergraduate Thesis, M. I. T., 1914.

[2] A. W. Porter, *Phil. Mag.*, **23**, 458, (1912).

been given a thorough test it is believed that it possesses interesting possibilities. Here the ordinates are the temperature of the liquid in question, while the abscissae are the temperatures at which some standard liquid has the same viscosity, and it will be noted that straight lines are obtained for most of the cases con-

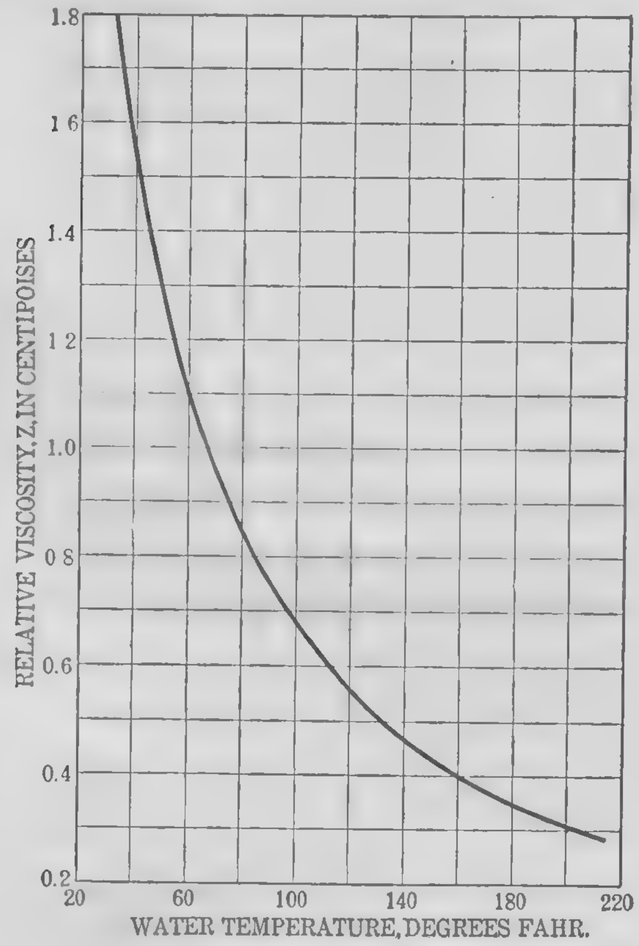


Fig. 24.—Viscosity of Water.

sidered. In this connection it is necessary to have data for standard liquids covering various ranges of viscosity, and a group of such curves is shown by Fig. 26. It is suggested that the standard liquid chosen for a given case be similar to the liquid with which it is being compared, *e.g.*, for aqueous solutions use an aqueous solution as the standard liquid, etc.

Herschel[1] has recently shown that Oelschläger's assumption of a straight line relationship between the logarithm of absolute viscosity and the logarithm of the temperature in degrees Fahrenheit is sufficiently accurate for practical purposes, "if only oils of medium viscosity are considered, excluding spindle and air-plane motor oils, as well as fatty, compounded, and unrefined oils." (See Fig. 27, p. 84.)

Porter[2] states that a rough parallelism exists at a given temperature between vapor pressure and fluidity (the inverse of viscosity). Thus liquid carbon dioxide has a very low viscosity while a high boiling petroleum oil is very viscous.

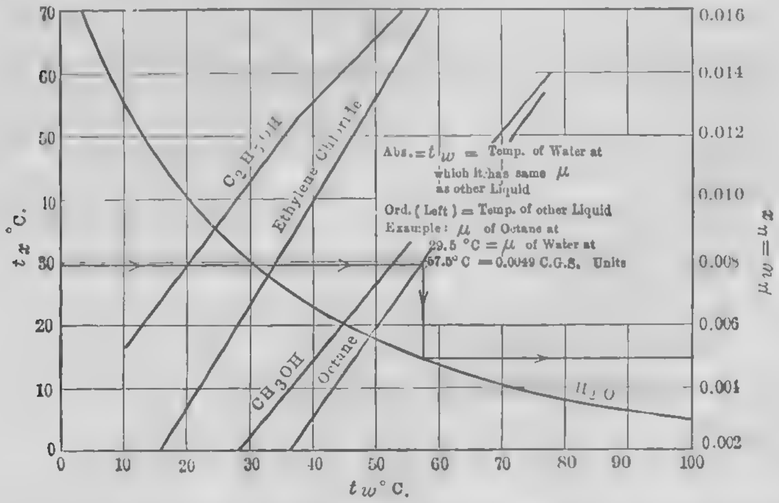

Abs. = t_w = Temp. of Water at which it has same μ as other Liquid
Ord. (Left) = Temp. of other Liquid
Example: μ of Octane at 29.5 °C = μ of Water at 67.5° C = 0.0049 C.G.S. Units
C_2H_5Cl
Ethylene Chloride
CH_3OH
Octane
H_2O
t_x °C.
t_w °C.
$\mu = n/n$

FIG. 25.—Porter's Method for Prediction of Change of Liquid Viscosity with Temperature.

As already stated, the viscosity of all liquids decreases with rise in temperature. This fact is of great importance in the pumping of oils. A certain crude oil at 120° F. has only $\frac{1}{16}$ its viscosity at 60° F. If the flow is straight line, by pumping at 120° F. the pressure drop will be reduced to $\frac{1}{16}$ the drop at 60° F. If the flow is turbulent, since f varies only as approximately the fourth root of z (see Fig. 28) the drop at 120° F. will be $\frac{1}{2}$ the drop at 60° F. Hence it is seen that the advantage of pumping

[1] *J. Ind. Eng. Chem.*, Vol. 14, No. 8, 715–723 (*Aug.* 1, 1922).
[2] A. W. PORTER, loc. cit.

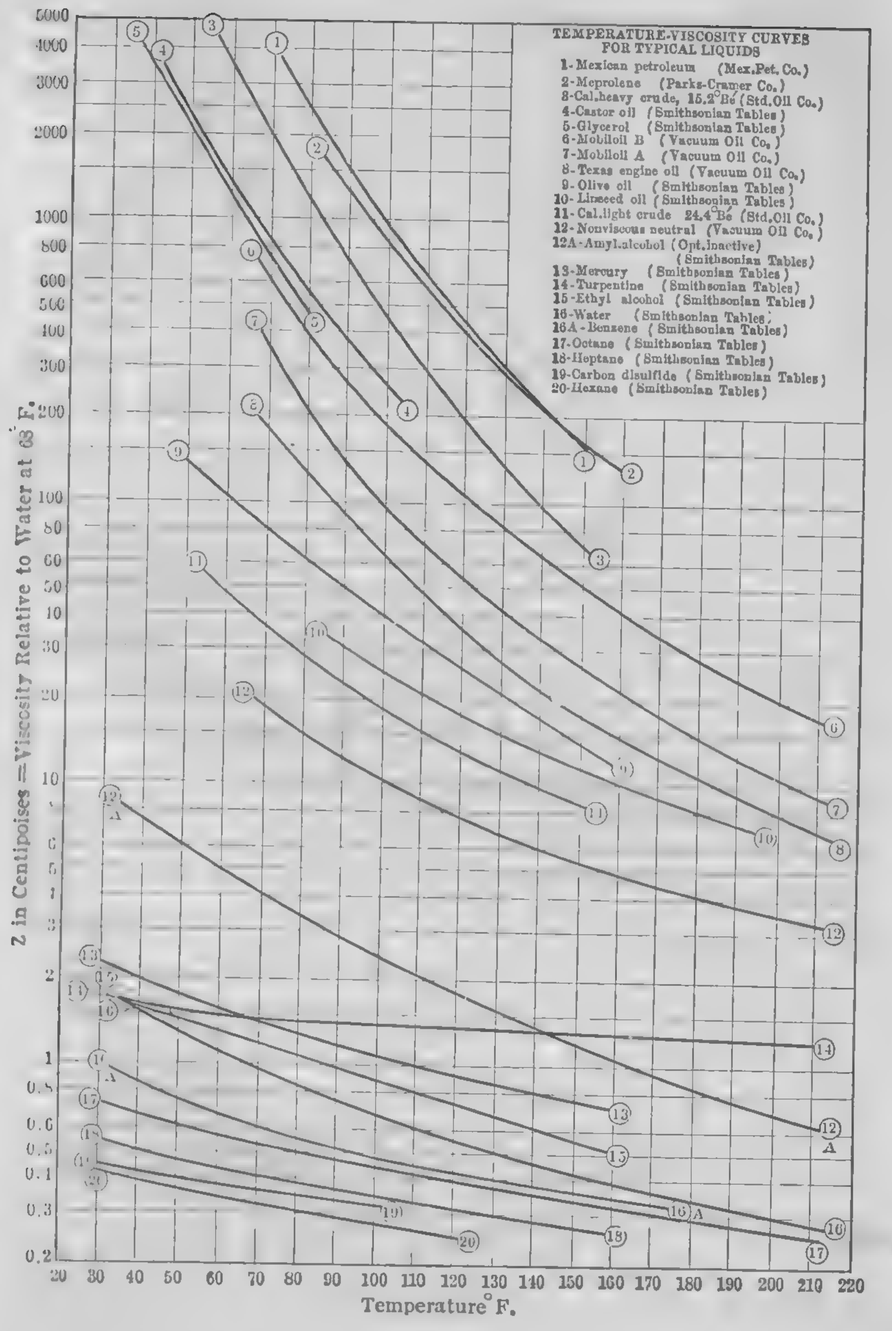

TEMPERATURE-VISCOSITY CURVES FOR TYPICAL LIQUIDS
1-Mexican petroleum (Mex.Pet. Co.)
2-Meprolene (Parks-Cramer Co.)
3-Cal.heavy crude, 15.2°Bé (Std.Oil Co.)
4-Castor oil (Smithsonian Tables)
5-Glycerol (Smithsonian Tables)
6-Mobiloil B (Vacuum Oil Co.)
7-Mobiloil A (Vacuum Oil Co.)
8-Texas engine oil (Vacuum Oil Co.)
9-Olive oil (Smithsonian Tables)
10-Linseed oil (Smithsonian Tables)
11-Cal.light crude 24.4°Bé (Std.Oil Co.)
12-Nonviscous neutral (Vacuum Oil Co.)
12A-Amyl alcohol (Opt.inactive) (Smithsonian Tables)
13-Mercury (Smithsonian Tables)
14-Turpentine (Smithsonian Tables)
15-Ethyl alcohol (Smithsonian Tables)
16-Water (Smithsonian Tables)
16A-Benzene (Smithsonian Tables)
17-Octane (Smithsonian Tables)
18-Heptane (Smithsonian Tables)
19-Carbon disulfide (Smithsonian Tables)
20-Hexane (Smithsonian Tables)
Viscosity Relative to Water at 68° F.
z in Centipoises = Viscosity
Temperature °F.

FIG. 26.[1]

[1] From *J. Ind. Eng. Chem.*, Vol. 14, No. 2, 105 (*Feb.* 1922).

hot instead of cold is greater if the flow be straight line in character rather than turbulent.

Conversion of Viscosity Units. In the c.g.s. system, the units for μ are

$$\frac{\text{(dynes per sq. cm.)}}{\text{(cm. per sec. per cm.)}} = \frac{\text{(second) (dynes)}}{\text{(sq. cm.)}}.$$

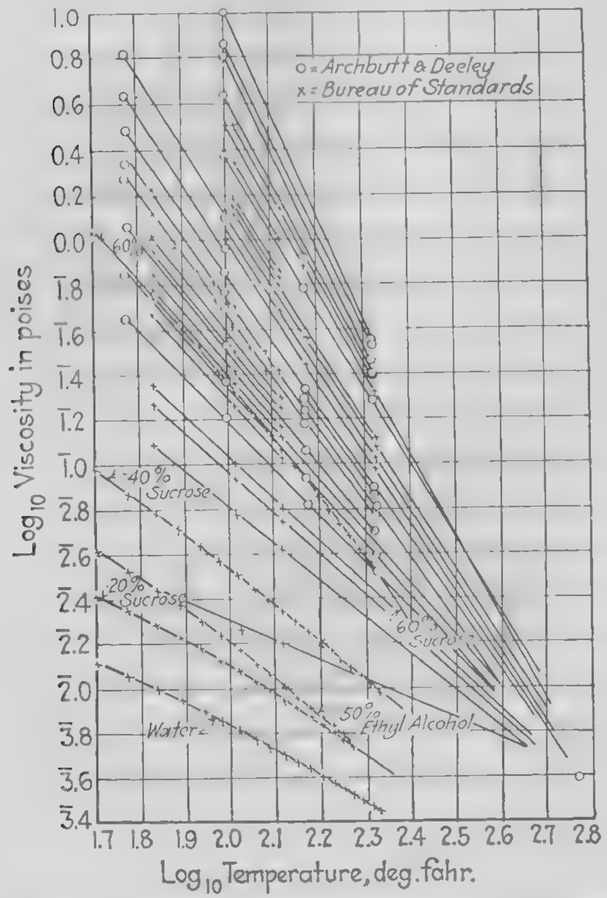


FIG. 27.—Logarithmic Viscosity-Temperature Diagram. Unless otherwise designated, the lines are for Paraffin Base Oils.

Since a dyne is a gram centimeter per sec. per sec., these units, reduce to (gms.)/(sec.) (cm.). Similarly, in the English system, the units of absolute viscosity are (sec.) (poundals)/(sq. ft.) or (lbs.)/(sec.) (ft.). Thus in order to convert absolute viscosity from the c.g.s. to the English system, it is necessary to convert (gms.)/(sec.) (cm.) to (lbs.)/(sec.) (ft.). The factor by which

the c.g.s. value must be multiplied to convert it to English units is, therefore, 30.5/454, or 0.0672. For example, the absolute viscosity of water at 68° F. (20° C.) is 0.0100 c.g.s. units (sometimes called "Poises") or (0.0100) (0.0672) = 0.000672 Eng. units.

The viscosity of a fluid relative to water at 68° F. is merely the *ratio* of its absolute viscosity to that of water at 68° F., both absolute viscosities being in the same units. Thus a liquid having an absolute viscosity at 150° F. of 0.200 c.g.s. units = (0.01344 Eng. units) has a relative viscosity of 0.200/0.0100 = 20, or 0.01344/0.000672 = 20.

The method of converting Saybolt seconds to relative viscosity has been given on page 79.

Friction Factors for Turbulent Motion.—When the velocity in question is above the critical value, it has been shown that the relation connecting the pressure drop and velocity is given by equation (38) for turbulent motion. This involves the friction factor f. In the past, engineers have employed various empirical equations showing f as a function of one or more of the following variables: inside diameter of pipe (d) in *feet*, average velocity of fluid (u) in *feet per second*, density of the fluid (ρ) as *lbs. per cu. ft.*, absolute viscosity of the fluid (μ) in *second poundals per sq. ft.*, and roughness of the surface (α).

Thus equations were obtained from which f for a *particular fluid* could be calculated, but they were limited to a certain definite range in variation of the particular variables employed. Often variables omitted from a given formula were quite important, thus making the value of f so calculated unreliable. Recently engineers have recognized the fact that the friction factor for any fluid is a function of all of the variables named above, *i.e.*, that $f = \phi_1(du\rho/\mu)$, $\varphi_2(\alpha/d)$.[1] Since it is not convenient to assign quantitative values to α/d, the relation between f and the modulus $du\rho/\mu$ is experimentally determined for pipes of a given range of relative roughness. For this reason the best correlation is obtained with data for smooth pipes. This relation was discovered[2] many years ago, but it was presented in such a man-

[1] The discussion is here confined to cases where the ratio of length to diameter is at least 200. For shorter pipes l/d must also be considered, but this effect may be allowed for by applying end corrections, as on pp. 90-91. See also HERSCHEL, *Proc. Am. Civil Eng.*, **84** (1921), 527.

[2] REYNOLDS, *Trans. Roy. Soc. London*, **1883,** 935; see also HELMHOLTZ, *Wissenschaftliche Abhandlungen*, I, 158, (1873).

ner that it has only recently been adopted by engineers. The most reliable accessible data on gases, water, and oils for turbulent flow in circular pipes have recently been correlated,[1] and it was found that all fluids having the same modulus give the same friction factor. The value of n (the slope of the curve obtained by plotting f versus $du\rho/\mu$ on logarithmic paper, as in Fig. 28), varies from about -0.4 to -0.2 or less, and for this reason it is most convenient to read the value of f from a plot of f as a function of the modulus. Since the authors of the paper just quoted were interested primarily in liquids, the modulus was given in terms of (Dus/z) instead of $(du\rho/\mu)$. The curves representing the most reliable data are shown in Fig. 28.

As stated above, when the flow is turbulent the modulus Dus/z is calculated and f is read from Fig. 28 and substituted in Eq. (38), $\Delta p = 4f\rho Lu^2/2gd$.

A glance at Eq. (38) for turbulent motion will show that it may be made to give the same result as Eq. (56) for straight line flow ($\Delta p = 32\mu Lu/gd^2$) by placing in Eq. (38) $f = \frac{16\mu}{du\rho}$. Since it is convenient in the case of liquids to deal with z, D and s instead of μ, d, and ρ, this expression for f, on substituting $\mu = 0.000672z$, $d = D/12$, and $\rho = 62.3s$, becomes $f = 0.00207z/Dus$. Thus Eq. (38) may be used for both turbulent and straight line flow, if in the case of the former f is determined by Fig. 28 and in the case of the latter f is determined by

$$f = 0.00207\frac{z}{Dus} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

Eq. (67)[2] has also been plotted on Fig. 28 so that for both types of motion f is read from Fig. 28 and is substituted directly into Eq. (38):

$$\Delta p = 4f\rho Lu^2/2gd.$$

By this method it is unnecessary to know which type of motion exists, but as a matter of interest, it will be turbulent if the abscissa falls to the right and straight line flow if the abscissa falls to the left of the intersection of the two lines on Fig. 28. This intersection for steel

[1] Wilson, McAdams, and Seltzer, *J. Ind. Eng. Chem.*, Vol. 14, No. 2, pp. 105 to 119 (1922).

[2] Where the line marked $f = 0.00207$ (z/Dus) on Fig. 28 runs off the plot to the left, f may be calculated by Eq. (67).

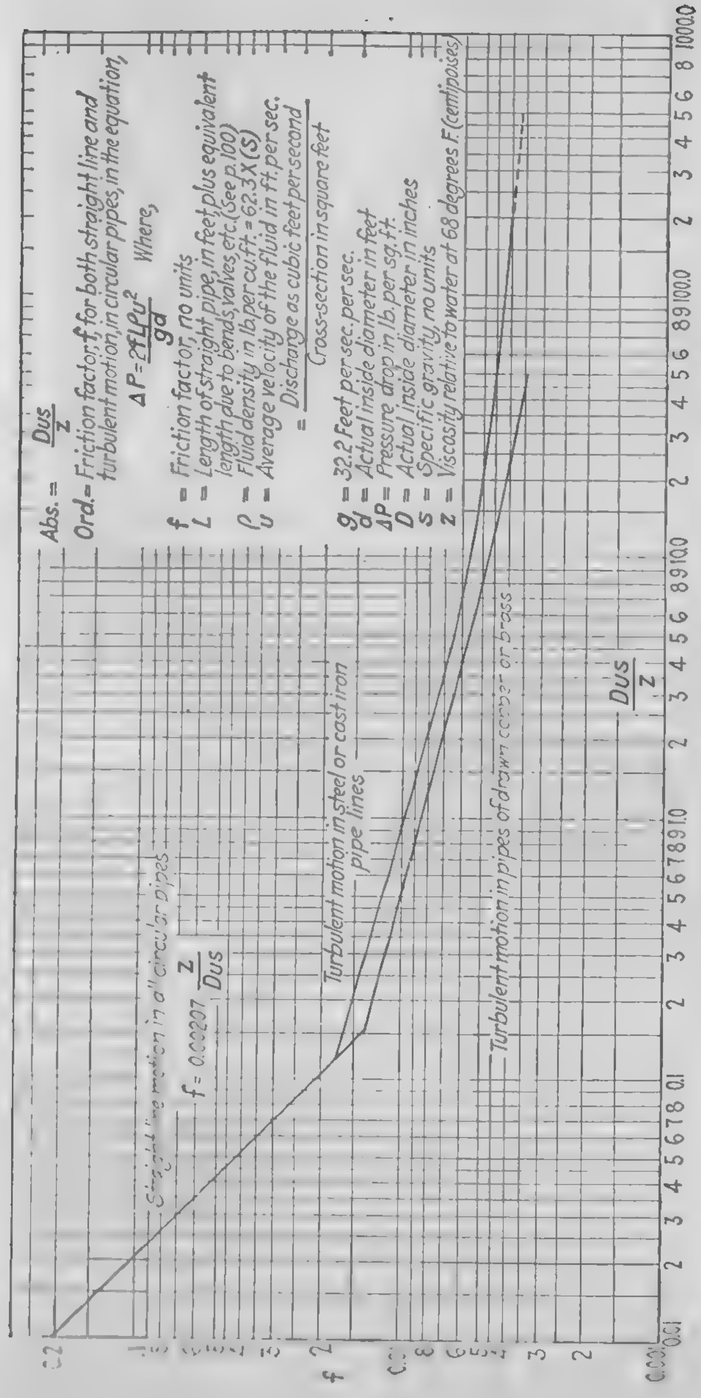

Abs. = Dus/z
Ord. = Friction factor, f, for both straight line and turbulent motion, in circular pipes, in the equation, ΔP = 2fLρu²/gd Where,
f = Friction factor, no units
L = Length of straight pipe, in feet, plus equivalent length due to bends, valves, etc. (See p. 100)
ρ = Fluid density in lb. per cu. ft. = 62.3 X (S)
u = Average velocity of the fluid in ft. per sec. = Discharge as cubic feet per second / Cross-section in square feet
g = 32.2 Feet per sec. per sec.
d = Actual inside diameter in feet
ΔP = Pressure drop in lb. per sq. ft.
D = Actual inside diameter in inches
S = Specific gravity, no units
z = Viscosity relative to water at 68 degrees F. (centipoises)
Straight line motion in all circular pipes
f = 0.00207 z/Dus
Turbulent motion in steel or cast iron pipe lines
Turbulent motion in pipes of drawn copper or brass
f
Dus/z

Fig. 28.[1]—Friction Factors for All Fluids in Circular Pipes.

[1] The curve for *turbulent* flow in steel pipes is based primarily on data for 1- to 4-in. pipes. For pipes smaller than 1 in., f should be increased by 10 per cent; for very large pipes, the curve shows conservatively high values, since the data for the large sizes approach closely the curve drawn for copper. The curve shown for viscous flow is correct for pipes of both copper and steel.

and cast-iron pipes is at $Dus/z=0.122$ and for drawn copper and brass pipes at $Dus/z=0.144$.

Illustration 8.—What is the pressure drop as pounds per square inch per mile of horizontal 6.07 i. d. steel pipe and the theoretical hp. required to transmit 1000 barrels of oil per hour if (z/s)[1] is (*a*) 50 and (*b*) 470? (One oil bbl. = 42 U. S. gals.; sp. gr. = 0.90.)

Solution.—(*a*) The average velocity through the pipe is

$$\frac{(42)\ (1000)}{(3600)\ (7.48)\ (6.07)\ (6.07)\ (0.785)/144} = 7.77 \text{ ft. per sec.}$$

The value of $Dus/z = (6.07)\ (7.77)/50 = 0.943$, and as shown in Fig. 28 the corresponding value of f is about 0.010.

By Eq. (38) the pressure drop per mile =

$$\frac{4f\rho Lu^2}{2gd} = \Delta p = \frac{(4)\ (0.010)\ (62.3)\ (0.9)\ (5280)\ (7.77)\ (7.77)}{(2)\ (32.2)\ (6.07)/(12)} =$$

21,900 lbs. per sq. ft. or (21,900/144) = 152 lbs. per sq. in. The theoretical power required to transmit the oil is determined by the c.f.p.m. and the intensity of pressure necessary to overcome friction and furnish the "velocity head." The latter term is

$$(7.77)\ (7.77)\ (62.3)\ (0.9)/(64.4) = 52.6 \text{ lbs. per sq. ft.,}$$

which is negligible in comparison to 21,900 lbs. per sq. ft. due to friction.

The theoretical power required

$$= \frac{(1000)\ (42)\ (21{,}900)}{(60)\ (7.48)\ (33{,}000)} = 62 \text{ hp. (theo.)}$$

The actual value will be the theoretical one divided by the efficiency of the pump.

(*b*) Here $Dus/z = (6.07)\ (7.77)/470 = 0.100$, and from Fig. 28, $f = 0.0207$.

Eq. (38) is used as before, even though the flow is now straight line instead of turbulent, and hence the pressure drop $= (152)\ \frac{(0.0207)}{(0.0100)} = 315$, which is 107 per cent higher than in case (*a*). Theoretical hp. = (2.07) (62) = 128.

[1] Referring to Eq. (65), p. 79, it is seen that the corresponding Saybolt viscosities would be 231 and 2140 seconds, respectively.

B. Sections other than Circular

For turbulent flow inside sections other than circular, the Fanning equation,

$$\Delta p = \frac{f\rho Lu^2}{2gm}, \quad \ldots\ldots\ldots \quad (38)$$

holds, the units being the same as those given under the preceding heading. Practically no data are available for the friction factor for sections other than circular, hence it is suggested that the hydraulic radius for the section in question be figured and multiplied by 4, giving the "equivalent diameter" of a circular pipe having the same hydraulic radius. The value of f, which is a function of Dus/z, is then read from Fig. 28, p. 87.

For straight line flow inside sections other than circular, equations are available for "annular sections" (such as the space between 2×3 in. std. double pipe coolers), and "parallel plates," such as the spaces between drier shelves. These equations are similar to Poiseuille's law for a circular pipe, and are given in the Summary of Equations, p. 94, together with the equations for critical velocity for flow through annular spaces and between parallel plates.

For the important case of the flow of air at right angles to staggered steam pipes as commonly used in so-called hot blast heaters, data are available for the relation between the total drop in pressure, the air velocity and the number of rows through which the air passes in series. The following approximate (empirical) equations have been derived from the data for Sturtevant[1] heaters. These data are used in the design of a hot blast heater, see pp. 158 to 159.

For 1-in. pipe (o. d. = 1.281 in.) on $2\frac{1}{8}$-in. centers (39.7 per cent "free area")[2]:

$$r = [0.000172 + 0.0000438N]u^2.$$

For 1-in. pipe (o. d. = 1.281 in.) on $2\frac{5}{8}$-in. centers (51.2 per cent "free area")[3]:

$$r = [0.000177 + 0.0000272N]u^2.$$

[1] "Data Book for Engineers and Architects," B. F. Sturtevant Co. Hyde Park, Mass., (1917).

[2] Refers to Sturtevant or Regular, London, and Mitre Types.

[3] Refers to Sturtevant Heaters of Mitre Type.

For 1-in. pipe (o. d.=1.281 in.) on $2\frac{3}{4}$-in. centers (55.3 per cent "free area");

$$r=[0.000174+0.0000251N]u^2.$$

Nomenclature:

r = inches of water;

u = average air velocity (reduced to 65° F. and normal barometer) through free area at center line at right angles to flow, expressed as feet per second.

N = Number of rows through which air passes in series.

NOTE.—These data cover a range of from 10 to 35 ft. per sec. and from 8 to 32 rows.

VI. CONTRACTION AND ENLARGEMENT LOSSES OF GASES AND LIQUIDS

Enlargement Loss. — When the cross-section is *suddenly* enlarged as shown in Fig. 29, a portion of the velocity pressure present in the upstream (smaller) section is transformed into static pressure in the downstream (larger) section, while the residual portion is lost due to the impact of the fast moving particles from the smaller section on the slow moving particles in the enlarged section.[1] The net result is that the downstream pressure is greater than the upstream, but is less than if there had been no loss. This "enlargement loss" is determined by the square of the difference of the velocities in the smaller and larger sections, as indicated by the following equation:

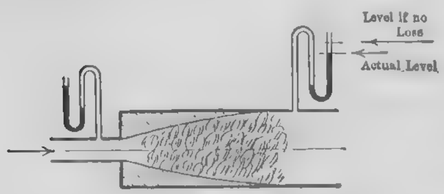


FIG. 29.—Enlargement Loss.

$$\Delta h=\frac{(u_1-u_2)^2}{2g}, \quad \ldots\ldots\ldots \quad (62)$$

where Δh is the lost head expressed in feet of fluid of the downstream density, u_1 and u_2 are the average fluid velocities as

[1] The fluid in the space outside the enlarging cone of moving fluid is substantially motionless; as indicated in Fig. 29.

feet/second at the upstream and downstream sections respectively, and g is 32.2 ft. per sec. per sec.

Contraction Loss.—When the cross-section is *suddenly* reduced as shown in Fig. 30, a portion of the static pressure present at the upstream (larger) section is transformed into velocity pressure in the downstream (smaller) section, while the residual portion is lost by impact. As shown diagrammatically the stream contracts from the cross-section at a–a to that at b–b and then enlarges from the cross-section at b–b to that at c–c. The *overall loss* from a–a to c–c is called the "contraction loss."

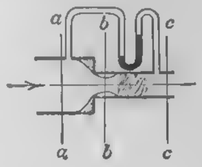


FIG. 30.—Contraction Loss.

The "contraction loss" is determined by the square of the fluid velocity in the smaller section and the ratio of areas of the smaller and larger areas as shown by the following equation,

$$\Delta h=\frac{K(u_2)^2}{2g}, \quad \ldots\ldots\ldots \quad (63)$$

where Δh is the lost head expressed as feet of fluid of the density existing at the downstream (smaller) section, u_2 is the fluid velocity as feet per second at the downstream (smaller) section, $g=32.2$ ft. per sec. per sec., and K decreases from 0.5 to 0 as the ratio A_2/A_1, the ratio of the downstream (smaller) area to the upstream (larger) area, increases from 0 to 1.0 as shown by Fig. 31.

Importance of Contraction and Enlargement Losses.—In many cases of turbulent motion the loss in pressure is due not only to the friction of the fluid flowing past the walls but also to the losses caused by sudden changes in the cross-sectional area of the path. It is important to be able to predict whether losses of the latter type may be neglected in comparison with the former. Calling x the number of contractions and y the number of enlargements (in general $x=y$), the total loss in head due to friction and sudden changes in cross-section is

$$(\Delta h)=\frac{fLu^2}{2gm}+(x)\ (K)\frac{(u_2)^2}{2g}+y\frac{(u_1-u_2)^2}{2g}.$$

Thus it is seen that in any particular case the relative magnitude of losses due to change in section to that due to friction is inde-

pendent of the velocity,[1] as long as the flow be turbulent. The main factor is seen to be the ratio of $(Kx+y)$ as compared to (fL/m). Hence in long conduits the contraction and enlargement

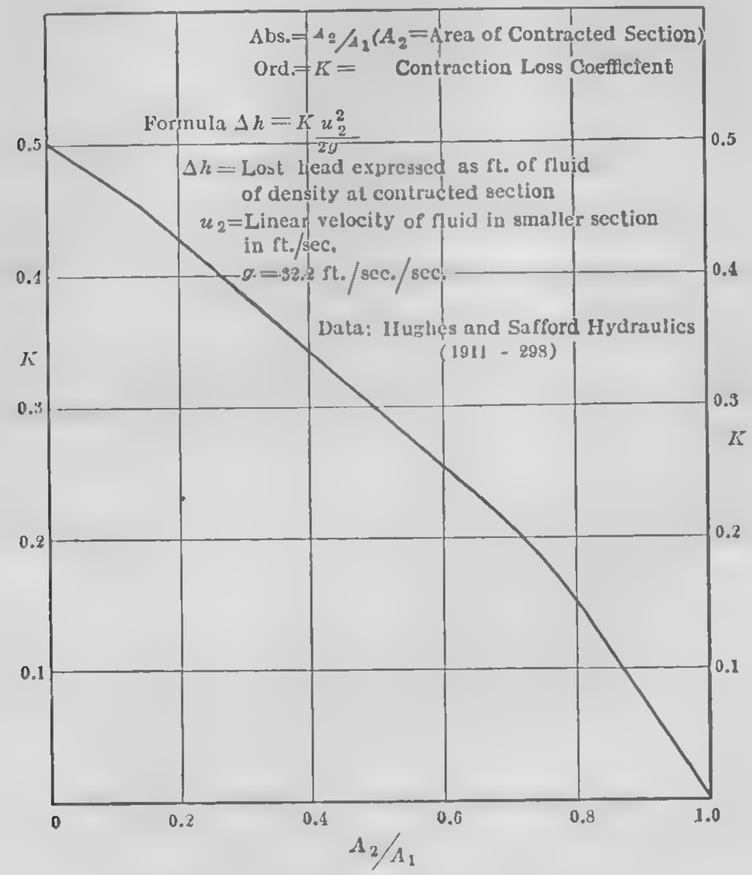


FIG. 31.—Coefficient in Contraction Loss Equation.

losses are negligible in comparison to the friction losses, whereas in many types of driers the friction loss may be almost negligible compared to the contraction and enlargement losses.

[1] It is obvious that the velocities at the various points may be expressed in terms of the velocity at any chosen section by means of area ratios.

SUMMARY OF EQUATIONS FOR FLOW OF GASES, VAPORS, AND LIQUIDS

PART I.—FOR GASES AND VAPORS WHERE PRESSURE DROP IS LESS THAN TEN PER CENT OF DOWNSTREAM ABSOLUTE PRESSURE AND FOR LIQUIDS FOR ALL PERCENTAGE PRESSURE DROPS.

I. Standard Orifice

When diameter of orifice chamber is at least 5 times that of orifice:

$$u_2 = c\sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where u_2 = average linear velocity through orifice.

For sharp-edged orifice (hole drilled in a $\frac{1}{16}$-in. to $\frac{3}{16}$-in. metal plate, or thicker plate beveled to a sharp edge, the beveled side being downstream), $c=0.61$. This does not apply where the thickness of the plate is appreciable compared to the diameter of the orifice.

For rounded orifice (hole drilled in a $\frac{1}{4}$-in. plate, the upstream edges being rounded accurately on a $\frac{3}{16}$-in. radius) $c=0.98$.

When diameter of orifice chamber is less than five times that of orifice:

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where c must be experimentally determined for the case in question.

NOTE.—Usually the drop through an orifice is *much* less than 10 per cent of the downstream absolute pressure; for an installation operated continuously it is generally uneconomical to have a high percentage drop.

II. Venturi Meter

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{2g(\Delta h)}. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

For well-made Venturi meters with proper angles of divergence and accurately bored throats, $c=0.98$.

III. Pitot Tube

For all pressures and readings

$$u_{act} = c\sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where u_{act} is the actual velocity at the point where reading is taken. For data concerning the ratio of the average velocity to that at the center line of the pipe, see p. 66.

The value of c ranges from unity for the type of instrument shown in Fig. 18, p. 63, to 0.84 for the more compact types.

IV. Pipes and Conduits

(*A*) *Turbulent Flow of Gases, Vapors and Liquids.*

$$\Delta h = \frac{(f)\ (L)\ (u)^{2*}}{(2)\ (g)\ (m)} = \frac{(2)\ (f)\ (L)\ (u)^{2\dagger}}{(g)\ (d)} \quad . \quad . \quad . \quad . \quad (38)$$

For values of f, see Fig. 28, p. 87.

(*B*) *Straight Line Flow for Gases, Vapors, and Liquids.*

For Circular Pipes:†

See Eq. (38) and Fig. 28, p. 87, also p. 100. If desired, the following may be used:

$$\Delta p = (\rho)\ (\Delta h) = \frac{(32)\ (\mu)\ (L)\ (u)}{(g)\ (d)^2} \quad . \quad . \quad . \quad . \quad . \quad (56)$$

Between concentric pipes:[1]

$$\Delta p = (\rho)\ (\Delta h) = \frac{8\mu L u}{g\left[r_2^2 + r_1^2 - \dfrac{(r_2^2 - r_1^2)}{ln_e \dfrac{r_2}{r_1}}\right]} \quad . \quad . \quad . \quad . \quad (57)$$

where r_2 and r_1 are the radii of the outer and inner boundaries, respectively, of the annular space.

For space between drier shelves (Parallel Plates):[1]

$$\Delta p = (\rho)\ (\Delta h) = \frac{(12)\ (\mu)\ (L)\ (u)}{(g)\ (a)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

(*C*) *Critical Velocity.*

As indicated by the solid lines in Fig. 22, p. 75, the pressure drop obtained is always the higher of the two possible values. Hence, below the critical velocity use equations for straight line flow; above the critical velocity use the equations for turbulent

* For flow through ducts of any cross-section; see p. 89.

† For flow through ducts of circular or square cross-sections only. This formula has been substantiated for the flow of air, steam, water and oils having a wide range of viscosities using commercial pipes from 1 in. to 12 in. in diameter.

[1] Equations from LAMB, "Hydrodynamics of Fluids," 3rd Ed., Cambridge Univ. Press (1906). No data are available to verify these equations.

flow. The equations for the critical velocity through various shaped sections are shown below:

For circular pipes:

$$u_c = \frac{16\mu}{f_c \rho d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

For space between concentric pipes:

$$u_c = \frac{8\mu(r_2 - r_1)}{f_c \rho \left[r_2^2 + r_1^2 - \dfrac{(r_2^2 - r_1^2)}{ln_e \dfrac{r_2}{r_1}}\right]} \quad . \quad . \quad . \quad . \quad . \quad (60)$$

For space between parallel plates:

$$u_c = \frac{12\mu}{f_c \rho a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

In all cases it will be noted that the equations show a high critical velocity for high viscosity, low density, and small diameter or clearance. Since f_c increases with the "roughness" of the pipe, the rougher the pipe, the lower will be the critical velocity.

V. Enlargement and Contraction Losses

For sudden enlargement in section:

$$\Delta h = \frac{(u_1 - u_2)^2}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

where u_1 and u_2 are the average velocities of fluid in feet per second in the smaller and larger sections, respectively.

For sudden contraction in section:

$$\Delta h = \frac{K u_2^2}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

where u_2 is velocity of fluid in feet per second in contracted section; K varies from 0.5 to 0, depending on the ratio of areas of contracted to original section, as shown in Fig. 31, p. 92.

VI. Work

$$\text{Theo. hp.} = \frac{(\Delta h)\ (G)}{550} = \frac{(\Delta p)\ (Q_2)}{550} = \frac{(\Delta h)\ (\rho)\ (Q_2)}{550}, \quad . \quad (64)$$

where Δh, ρ, and Q_2 are expressed in terms of the *downstream* density. The *actual* work is obtained by dividing the above by the mechanical efficiency of the fan, exhauster, or blower.

Part II. For Gases and Vapors, where Pressure Drop Exceeds 10 Per Cent of Downstream Absolute Pressure (for Liquids: See Part I).

I. *A.* Standard Orifice, Gases and Vapors, Chamber Diameter is at Least Five Times Orifice Diameter

Pressure drop is 10 per cent to 20 per cent of downstream absolute pressure:

$$u_2 = c\sqrt{(2)\ (g)\ (b)\ (T)\left(ln_e\frac{p_1}{p_2}\right)}. \quad . \ . \ . \quad (13)^1$$

Pressure drop is over 50 per cent of upstream absolute pressure:

$$G = cAp_1\sqrt{\frac{Mgk}{BT}\left[\left(\frac{1+k}{2}\right)^{\frac{1+k}{1-k}}\right]}, \quad . \ . \ . \quad (25a)^1$$

where downstream pressure, p_2, must be less than $p_1\left(\frac{2}{1+k}\right)^{\frac{k}{k-1}}$.

Thus for the permanent diatomic gases and steam the downstream absolute pressure must be less than 53 per cent and 55 per cent, respectively, of the initial absolute pressure.

Since k for air is 1.404, (25a) becomes

$$G = \frac{(0.533)\ (c)\ (A)\ (p_1)}{\sqrt{T_1}} \quad (\textit{Fliegner's Equation}). \ . \quad (26)^1$$

For steam (19) becomes approximately

$$G = \frac{cAp_1}{70}. \quad (\textit{Napier's Equation}). \ . \ . \ . \quad (27)^1$$

I. *B.* Standard Orifice, Gases and Vapors, Chamber Diameter Less than Five Times that of Orifice

For any percentage pressure drop:

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{\frac{(2)\ (g)\ (k)\ (p_1)\ (v_1)}{(k-1)}\left[1-\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]}. \ . \quad (11)$$

Value of c should be experimentally determined for the conditions existing.

[1] For values of c, see Part I of Summary.

II. Venturi Meter

For Gases and Vapors:

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{(2)\ (g)\ (b)\ (T)\left(ln_e\frac{p_1}{p_2}\right)}. \ . \ . \ . \quad (7)$$

Note.—For values of c, see Part I of Summary.

III. Pitot Tube

For gases, vapors and liquids, and for all percentage pressure drops, use same equations as given under Part I of Summary.

IV. Pipes and Conduits

A. Turbulent Flow (Gases and Vapors).

For any cross-sectional shape of length less than 200 diameters but not extremely short:

$$u_1 = \sqrt{\frac{(g)\ (B)\ (T)\ (p_1^2 - p_2^2)/(2)\ (M)\ (p_1)^2}{\left[\left(\frac{f\,L}{2\,m}\right)+\left(ln_e\frac{p_1}{p_2}\right)\right]}} \quad . \ . \quad (51a)$$

$$G = A\sqrt{\frac{gM\ (p_1^2 - p_2^2)/2BT}{\left[\left(\frac{fL}{2m}\right)+\left(ln_e\frac{p_1}{p_2}\right)\right]}} \quad . \ . \ . \ . \ . \ . \ . \quad (51c)$$

For any cross-section of length at least 200 diameters long:

$$u_1 = \sqrt{\frac{(g)\ (m)\ (B)\ (T)\ (p_1^2 - p_2^2)}{(M)\ (p_1^2)\ (f)\ (L)}} \ . \ . \ . \ . \ . \ . \ . \quad (52a)$$

$$G = A\sqrt{\frac{gmM\ (p_1^2 - p_2^2)}{BTfL}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (52c)$$

Note.—For values of f, see Fig. 28, p. 87. Do not apply these equations to extremely short tubes or orifices, as these equations ignore entrance and exit losses. To allow for bends, valves, etc., see Table II and Fig. 32, p. 100.

B. Straight Line Flow (Gases and Vapors).

No equation is given for this case as it is not found in practice.

V. Work

For gases and vapors, adiabatic compression:

$$\text{Theo. hp.} = \frac{G(k)\ (p_1v_1)}{(550)\ (k-1)}\left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} - 1\right] \quad . \ . \ . \quad (11)$$

NOTE.—This is the sum of the compression and expulsion work, less admission work. Actual hp. of compressor or blower is theoretical value divided by mechanical efficiency.

Nomenclature

Explanation of Subscripts

1 refers to *upstream* section.
2 refers to *downstream* section.
act. refers to *actual.*
max. refers to *maximum.*
c refers to *condition* at the *critical velocity.*
s refers to a *standard* liquid.
x refers to any liquid other than the standard one.
w refers to *water.*

Explanation of Symbols (English Units)

A = Area of cross-section in *sq. ft.*
a = Clearance between drier shelves or between concentric pipes, *in feet.*
B = "Gas constant" = 1544; $pv = BT/M = bT$.
b = Constant in gas law = $B/M = 1544/M$.
c = Coefficient of discharge.
d = Inside pipe diameter in *feet.*
D = Inside pipe diameter in *inches.*
E = Intrinsic energy per lb. of fluid = B.t.u. content above 32° F.
f = Friction factor (*no units*). (See Fig. 28 for values.)
g = 32.2 *ft. per sec. per sec.*
G = Rate of flow of fluid as *pounds per second.*
h = Fluid head expressed in *feet* of fluid flowing.
Δh = Differential head and pressure drop, *expressed in feet of the fluid of downstream density* = $h_1 - h_2 = \Delta p/\rho$.
H = Heat imparted to a flowing fluid from an external source, in *foot-pounds per pound* of fluid.
k = Ratio of specific heat at constant pressure to specific heat at constant volume. (See Table I, p. 99, for values.)
K = Coefficient in contraction loss equation. (See Fig. 31, p. 92, for values.)
L = Frictional length in *feet* = actual length of straight pipe plus equivalent length due to valves, bends, etc., expressed in feet. For values of equivalent lengths, see Table II and Fig. 32, p. 100,
M = Average molecular weight (*no units*). For air, $M = 29$.
m = Hydraulic radius in *feet* = area of clear cross-section in square feet/"wetted" perimeter of section in feet = cu. ft. clear volume/sq. ft. "wetted" perimeter.
n = Rate of flow of fluid as *pound mols per second.*
ln = Logarithm to the "natural" base $e = 2.3$ times logarithm to the base 10.
p = Absolute pressure in *lbs. per sq. ft.*
$\Delta p = p_1 - p_2$ = differential pressure and pressure drop. Expressed in *lbs. per sq. ft.* = $(\Delta h)\ (\rho)$.
Q_2 = Rate of flow of fluid as *cubic feet (measured at downstream density) per second* = Q.

R = Mechanical work imparted to a flowing fluid from an external source, *foot-pounds per pound* of fluid.
s = Specific gravity of fluid at temperature in question relative to water at room temperature (*no units*).
T = °*F. absolute temperature* = °F. + 460 = (1.8) (°C. absolute).
u = Average linear fluid velocity in *feet per second.*
u_{act} = *Actual* velocity in *feet per second* where the point of Pitot tube is inserted. This is *not* the average velocity.
u_{max} = *Maximum* velocity of fluid as *feet per second.*
u_c = *Critical* (average) velocity of fluid in *feet per second.*
v = Specific volume of fluid = $1/\rho$ = *cu. ft. per lb.*
$W = \int p dv$ = Work of expansion, *foot-pounds per pound* of fluid.
x = Potential head, in *feet* above datum.
z = Relative viscosity of fluid at temperature in question, referred to (liquid) water at 68° F. = *centipoises.*

Explanation of Greek Symbols

μ = Absolute viscosity of fluids in English units (*lbs. per sec. per ft.*) or (poundals) (sec.)/(sq. ft.) = absolute viscosity in c.g.s.[1] units, (gms.)/(sec.)/cm., or (sec.) (dynes)/(sq. cm.), multiplied by 0.0672. For liquids, μ (in Eng. units) = 0.000672z.
μ_w = Absolute viscosity of water in English units. See Fig. 24, p. 81, for data, and p. 85 for conversion factors.
ρ = Fluid density as *lbs. per cu. ft. at downstream section*; (at room temp. = 62.3s).
θ = Time in any convenient unit.

TABLE I

AVERAGE VALUE OF "k" (RATIO OF SPECIFIC HEAT OF GASES AND VAPORS AT CONSTANT PRESSURE TO SPECIFIC HEAT AT CONSTANT VOLUME)[2]

	k
Monatomic Gases (A, He, Hg)	1.667
Permanent Diatomic Gases (Air, O_2, N_2, H_2, CO)	1.405
Hydrochloric Acid Vapor (HCl)	1.40
Chlorine Vapor (Cl_2)	1.36
Carbon Dioxide (CO_2)	1.30
Sulphur Dioxide (SO_2)	1.26
Steam (H_2O Vapor)	1.28
Ammonia Vapor (NH_3)	1.30
Methane (CH_4)	1.31
Acetylene (C_2H_2)	1.26
Ethylene (C_2H_4)	1.24
Ethane (C_2H_6)	1.22
Carbon Bisulphide (CS_2)	1.20
Benzol (C_6H_6)	1.10
Ethyl Ether ($C_4H_{10}O$)	1.08

[1] This c.g.s. unit of viscosity is sometimes called a "poise." Water at 20° C. has an absolute viscosity of 0.010 "poises," or 1.0 centipoise.

[2] Taken from various sources in the literature.

TABLE II

EQUIVALENT LENGTHS, EXPRESSED AS DIAMETERS OF ADDITIONAL STRAIGHT PIPE (For *turbulent* motion)

90° Elbows,[1]	1 in. to 2½ in.	30
	3 in. to 6 in.	40
	7 in. to 10 in.	50
Globe Valve,[1]	1 in. to 2½ in.	45
	3 in. to 6 in.	60
	7 in. to 10 in.	75
Tees,[2]	1 in. to 4 in, full size branch	60
90° Curves,[3] same inside dia. as pipe:		
	center line radius = dia. of pipe	20
	center line radius = 2 to 8 dia.	10
Square Elbow,[2] (intersection of two cylinders)		50
Entrance loss, See p. 91		
Exit loss, See p. 90		

[1] E. MILLER, "Notes on Heating and Ventilating," M. I. T.

[2] MARKS, "Mechanical Engineers' Handbook," McGraw–Hill, N.Y. (1916).

[3] *Trans. Am. Soc. C. E.*, **62,** pp. 67 to 112 (1909).

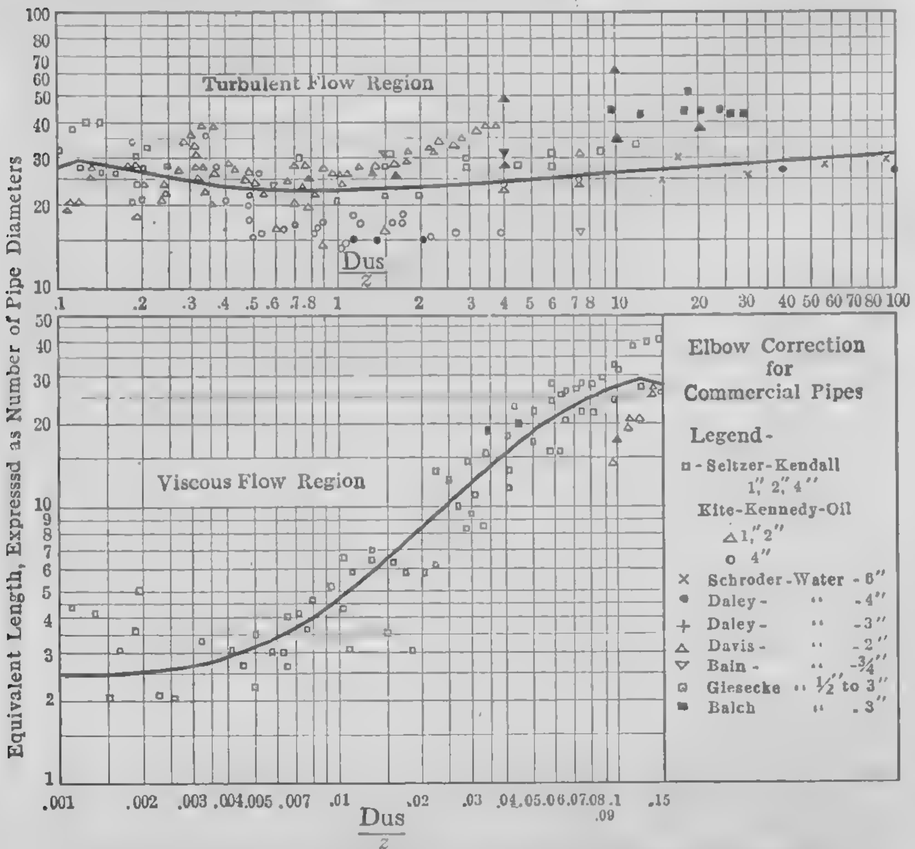

Turbulent Flow Region
Viscous Flow Region
Equivalent Length, Expressd as Number of Pipe Diameters
Dus / z
Elbow Correction for Commercial Pipes
Legend -
□ - Seltzer - Kendall 1", 2", 4"
Kite - Kennedy - Oil △ 1", 2" o 4"
× Schroder - Water - 6"
• Daley - " - 4"
+ Daley - " - 3"
△ Davis - " - 2"
▽ Bain - " - ¾"
⊡ Giesecke " ½" to 3"
■ Balch " - 3"

FIG. 32.—Equivalent Frictional Lengths of Standard 90°-Elbows.

WILSON, MCADAMS, and SELTZER, *J. Ind. Eng. Chem.*, Vol. 14, No. 2, 105-110 (Feb., 1922).

TABLE III

STANDARD FULL-WEIGHT WROUGHT-IRON AND STEEL PIPE
(National Tube Company)

Nominal diameter, inches	Actual external diameter, inches	Approximate internal diameter, inches	Nominal weight per foot, pounds	Number of threads per inch of screw
⅛	0.405	0.27	0.24	27
¼	0.540	0.36	0.42	18
⅜	0.675	0.49	0.57	18
½	0.840	0.62	0.85	14
¾	1.050	0.82	1.13	14
1	1.315	1.05	1.68	11½
1¼	1.660	1.38	2.27	11½
1½	1.900	1.61	2.72	11½
2	2.375	2.07	3.65	11½
2½	2.875	2.47	5.79	8
3	3.500	3.07	7.57	8
3½	4.000	3.55	9.11	8
4	4.500	4.03	10.79	8
4½	5.000	4.51	12.54	8
5	5.563	5.05	14.62	8
6	6.625	6.07	18.97	8
7	7.625	7.02	23.54	8
8	8.625	8.07	24.69	8
8	8.625	7.98	28.55	8
9	9.625	8.94	33.91	8
10	10.750	10.19	31.20	8
10	10.750	10.14	34.24	8
10	10.750	10.02	40.48	8
11	11.750	11.00	45.56	8
12	12.750	12.09	43.77	8
12	12.750	12.00	49.56	8
13	14.000	13.25	54.57	8
14	15.000	14.25	58.57	8
15	16.000	15.25	62.58	8

DERIVATION OF EQUATIONS FOR THE FLOW OF FLUIDS

Simplification of Bernoulli's Theorem.

As given in the introduction of this chapter, the form of Bernoulli's theorem most frequently used for 1 lb. of fluid is:

$$x_1+p_1v_1+\frac{{u_1}^2}{2g}+R+W=x_2+p_2v_2+\frac{{u_2}^2}{2g}+F. \quad . \quad (2)^1$$

As has been stated, all terms in this equation are mutually convertible, are expressed in the same units, *i.e.*, feet of fluid flowing, and are called "heads." This equation is the mathematical statement of the equality of the sum of all forms of mechanical energy possessed by the fluid at one section of a continuous system and of all forms at a second section, corrected for such energy received or dissipated between the two sections.

In all equations which follow, for the sake of simplicity, the term R has been omitted, inasmuch as the mechanical work added by a pump is best considered separately. In deriving equations F is also omitted, but allowance for friction is made wherever necessary.

It is impossible to use Eq. (2) unless one is able to evaluate the term, $W=\int pdv$. This can be done only when the functional relation between p and v is available for the conditions involved. One must always know the equation of state of the fluid and furthermore have definite information as to the external conditions imposed upon it. The following important special cases are frequently met in industrial practice.

(a) *Flow at Constant Temperature.*—Liquids and gases are usually transported at atmospheric temperature, and most instruments for measuring the rate of flow are operated under isothermal conditions. Now, in the case of perfect gases, owing to the constancy of the "pv-product" at constant temperature, the pv-term disappears. In the case of liquids, since these are practically incompressible, the specific volume remains constant, and W becomes zero.

[1] The form of this equation is equivalent to defining friction as the disappearance of mechanical energy as such; it must of course reappear as heat. This definition is in a sense arbitrary, but is justified by the experimentally determined fact that no such conversion occurs except where relative motion exists and always follows the friction laws developed on pp. 73–92, 110–116.

Thus, for isothermal flow of *perfect gases* the general form of Bernoulli's theorem is,

$$x_1+{u_1}^2/2g+W=x_2+{u_2}^2/2g \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

For the isothermal flow of *liquids*, $v_1=v_2=1/\rho$, $W=0$, and hence (2) becomes,

$$x_1+\frac{p_1}{\rho}+\frac{{u_1}^2}{2g}=x_2+\frac{p_2}{\rho}+\frac{{u_2}^2}{2g}. \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

(*b*) *When Change in Potential Head is Negligible.*—Gases and vapors are usually moved at velocities a great deal higher than liquids, and the W-term is usually much greater. In consequence, the x-term which appears only when the direction of flow is not horizontal, becomes of relatively little importance, and can often be neglected. When a differential gauge is used in determining the pressure differences, as is usually the case for gases, the two values of x automatically balance each other, giving

$$\frac{{u_1}^2}{2g}+W=\frac{{u_2}^2}{2g}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2c)$$

All of these simplifications, each allowable under special conditions, result in modifications of Bernoulli's theorem, thus changing its appearance, and use. These special cases will be discussed in detail in the following order:

A. Gases and Vapors.

Introduction (Adiabatic versus Isothermal Flow).
- (I*a*) Standard Orifice (Small Percentage Pressure Drop).
- (I*b*) Standard Orifice (Large Percentage Pressure Drop).
- (II) Venturi Meter.
- (III) Pitot Tube.
- (IV*a*) Flow of Gases through Conduits of Constant Cross-section (Turbulent Flow).
- (IV*b*) Flow of Gases through Conduits (Straight Line Flow).

B. Water.
- I. Standard Orifice.
- II. Venturi Meter.
- III. Pitot Tube.
- IV. Flow through Conduits of Constant Cross-section.

C. Liquids other than Water.
I. Flow through Circular Pipes.

D. Enlargement and Contraction Losses for all Fluids.

A. DERIVATION OF EQUATIONS FOR GASES AND VAPORS

Isothermal vs. Adiabatic Flow of Perfect Gas.

Neglecting differences in potential heads, Bernoulli's theorem for compressible fluids (2) becomes

$$u_2^2/2g - u_1^2/2g = p_1v_1 - p_2v_2 + W \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Assuming the perfect gas law,

$$pv = bT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the work of expansion at constant temperature is

$$W = \int_{v_1}^{v_2} pdv = p_1v_1\, ln^1(p_1/p_2), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$p_1v_1 = bT = p_2v_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Then for the *isothermal* flow of a perfect gas, (3) becomes

$$u_2^2/2g - u_1^2/2g = p_1v_1 ln(p_1/p_2) = bT ln(p_1/p_2). \quad . \quad . \quad (7)$$

When a perfect gas expands under conditions where there is no heat interchange between the gas and its surroundings, the expansion is said to be "adiabatic" and the pressure volume relations for an adiabatic change are

$$p_1(v_1)^k = p_2(v_2)^k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k is the ratio of the specific heat of the gas at constant-pressure to that at constant volume; employing (8), the integral of pdv for an *adiabatic expansion becomes*

$$\int_{v_1}^{v_2} pdv = \frac{p_1v_1}{k-1}[1-(p_2/p_1)^{(k-1)/k}], \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$p_1v_1 - p_2v_2 = p_1v_1[1-(p_2/p_1)^{(k-1)/k}] \quad . \quad . \quad . \quad . \quad . \quad (10)$$

[1] *ln* represents "natural logarithm, *i.e.*, the logarithm to the base *e*.

Substituting (9) and (10) in (3), there results the integrated equation for the *adiabatic flow of a perfect gas*

$$\frac{u_2^2}{2g} - \frac{u_1^2}{2g} = \frac{(p_1v_1)}{k-1}\frac{(k)}{}[1-(p_2/p_1)^{(k-1)/k}] \quad . \quad . \quad . \quad . \quad (11)$$

Since equations developed later are based on assumptions of isothermal or adiabatic flow, it is evident that equations (7) and (11) are fundamental. The ratio of these two expressions is

$$\frac{(k-1)\ ln\ (p_1/p_2)}{k[1-(p_2/p_1)^{(k-1)/k}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Where there is no pressure drop, that is, where $p_2 = p_1$, the ratio (12) may be shown by the calculus to be unity. In other words, where the pressure drop is negligible, the velocity changes are practically identical for isothermal or adiabatic flow. So nearly coincident are the isothermal and adiabatic curves that even though the pressure change be 20 per cent of the initial pressure, the difference in the velocity changes for the two curves is only 1 per cent; that is, isothermal expansion represents the results within the experimental error. Wherever the pressure change is less than 20 per cent, the assumption of isothermal expansion is entirely justified and should be employed because the expressions and calculations involved are simplified.

Ia. *Standard Orifice, Low Percentage Pressure Drop.*—With suitable orifice chambers, as described on p. 55, the equation for isothermal flow (7) becomes

$$u_2^2/2g = bT ln_e(p_1/p_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If $ln\ (1+y)$ be expanded by Maclaurin's theorem, it gives $y - y^2/2 + y^3/3 - y^4/4$, etc., and if y be small as compared with unity, this series is sensibly equal to y itself. Since p_1 is very nearly equal to p_2, the logarithm of p_1/p_2 may be written as

$$ln\left[1+\left(\frac{p_1}{p_2}-1\right)\right], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which, since the term $\frac{p_1}{p_2}-1$ is small compared to unity, is nearly equal to $\frac{p_1}{p_2}-1$ itself or to $\frac{p_1-p_2}{p_2}$[1].

[1] This simplification leads to errors of +1.1 per cent where p_1 is 2 per cent

Substituting $\frac{p_1-p_2}{p_2}$ for $ln\ (p_1/p_2)$ in (13), there results

$$u_2^2/2g=bT(p_1-p_2)/p_2. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Since by the gas laws $bT/p_2=v_2$, (15) becomes

$$u_2=\sqrt{2gv_2(p_1-p_2)}=\sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad (16)$$

where Δh is the differential reading expressed in feet of fluid having the same density as the gas on the downstream side of the orifice. In practice this differential head is measured in feet of some liquid, and the reading is multiplied by the ratio of the density of the liquid to that of the gas at the *downstream* temperature and pressure.

The observed flow in cubic feet per second (Q_2) of the downstream density is always less than is called for by Eq. (16), since in practice there is a friction loss which reduces the calculated velocity, and the issuing stream does not have a cross-section as large as the orifice. These facts necessitate the use of a coefficient of discharge, c.

$$Q_2=cA\sqrt{2g(\Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Calling the average velocity through the orifice u_2, since $Q_2=Au_2$

$$u_2=c\sqrt{2g(\Delta h)}=c\sqrt{2gv_2(p_1-p_2)}=c\sqrt{\frac{2gBT(p_1-p_2)}{Mp_2}}. \quad . \quad (18)$$

If the chamber diameter be small compared to that of the orifice, one obtains

$$\sqrt{u_2^2-u_1^2}=c\sqrt{2g\ (\Delta h)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

I*b*. *Standard Orifice, High Percentage Pressure Drop.*—The assumption of isothermal flow no longer holds when the percentage pressure drop across an orifice becomes high, and the theoretically correct adiabatic equation (11) must be employed. As above, with a large orifice chamber the square of the velocity in the chamber can be neglected when compared to the square

greater than p_2, +5.2 per cent where p_1 is 10 per cent greater than p_2, and +9.8 per cent where p_1 is 20 per cent greater than p_2. Usually the drop is less than 1 per cent.

of the velocity in the orifice. Introducing the coefficient of discharge as before,

$$u_2=c\sqrt{\frac{2gk(p_1v_1)}{k-1}[1-(p_2/p_1)^{(k-1)/k}]}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$Q_2=cA\sqrt{\frac{2gkp_1v_1}{k-1}[1-(p_2/p_1)^{(k-1)/k}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$G=Q_2/v_2=cA\sqrt{\frac{2gk\ \ p_1}{(k-1)(v_1)}[(p_2/p_1)^{2/k}-(p_2/p_1)^{(1+k)/k}]} \quad . \quad (22)$$

This equation applies to the flow of gases through orifices under a drop in pressure large compared to the total pressure, but is seldom used for calculations in the form given above, since, under properly chosen conditions the flow can be calculated by a less complicated equation. It is self-evident that the transition from isothermal to adiabatic flow, produced as it is by increase in pressure drop through the orifice cannot be a sharp one, and it is therefore highly probable that intermediate values of the pressure drop will not satisfactorily follow either equation. It has been proposed to take care of such by an intermediate constant, n, instead of the ratio of the specific heats of the gases, k, in the equation for adiabatic flow, as is done in the calculation of the work consumption of air compressors, but on the other hand, the complications involved in such a correction are so great that engineers in general have never adopted the suggestion.

The expression (22) for adiabatic flow contains the function

$$[(p_2/p_1)^{2/k}-(p_2/p_1)^{(1+k)/k}]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Where there is no flow through the orifice, $p_2/p_1=1$, and as the ratio of p_2/p_1 decreases from unity, the quantity (23) and consequently the flow given by Eq. (22), increases from zero, reaching a maximum when

$$p_2/p_1=\left(\frac{2}{1+k}\right)^{k/(k-1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

After p_2/p_1 falls below the "critical" value given by (24) which calls for maximum flow, the flow should decrease according to Eq. (22). Experiments have shown that the flow does correspond to Eq. (22) above and at the critical pressure ratio, but that

it remains constant for further decrease in the pressure ratio. This apparent discrepancy is explained as follows. Until the critical downstream pressure is reached, the throat and downstream pressures are the same, but as the downstream pressure (p_2) is further decreased the throat pressure (and velocity also)[1] remain constant, and since the throat pressure is the controlling factor, the rate of flow remains unchanged.[2] Therefore, (23) has a constant value when the pressure ratio of p_2/p_1 is not greater than the critical value given by Eq. (24), and under such conditions the general equation for adiabatic flow (22), which assumed a large orifice chamber, reduces to

$$G = cA\, p_1 \sqrt{\frac{gkM}{BT}\left[\left(\frac{1+k}{2}\right)^{\left(\frac{1+k}{1-k}\right)}\right]}, \quad . \quad . \quad . \quad . \quad (25a)$$

or

$$n = cA\, p_1 \sqrt{\frac{gk}{BMT}\left[\left(\frac{1+k}{2}\right)^{\left(\frac{1+k}{1-k}\right)}\right]}. \quad . \quad . \quad . \quad . \quad (25b)$$

Since k for air is 1.405 (25a) becomes

$$G = 0.533 cA p_1/\sqrt{T_1} = \text{lbs. air per sec.}, \quad . \quad . \quad (26)$$

where the downstream pressure is not greater than 0.53 times the initial pressure above the orifice, and, as before, where the area of the orifice chamber is at least 25 times that of the orifice. This special case is known as *Fliegner's Equation*. For steam, k increases with T in such a way that (approximately) they offset each other in Eq. (25a), which reduces (approximately) to the well-known *Napier Equation* for saturated steam, when the absolute back pressure is less than 55 per cent of the initial absolute pressure:

$$G = \frac{cAp_1}{70}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

[1] This argument assumes constancy of initial pressure.

[2] A gas flowing from a high pressure through a small orifice to a low pressure can be conceived as passing through two stages. In the first stage, the gas has its velocity increased to that in the throat of the orifice, this increase in velocity corresponding to a drop in pressure of the gas. The second stage involves the passage of the gas from the throat of the orifice into the low-pressure (downstream) orifice chamber. If the velocity in the throat be not too great, the pressure drop in the second stage is negligible, but if the velocity in the throat be increased, a point is finally reached beyond which the gas cannot dissipate itself from the throat into the low-pressure chamber fast enough to lower the throat pressure further. The throat pressure will then remain constant, independent of the pressure in the low-pressure chamber.

Inasmuch as these simple equations (25a, 25b, 26 and 27) hold whenever the pressure ratio is sufficiently low and the orifice chamber is sufficiently large compared to the orifice, it is highly desirable whenever possible to secure these conditions where the percentage drop in pressure is large; as above stated for air and other permanent diatomic gases,[1] this pressure ratio should be below 0.53, and for steam below 0.55. Values of the coefficient (c) for various types of orifices are given on p. 93. For the most accurate work, the orifice in question must be standardized. Attention should be called to the fact that the coefficient, c, in the case of a rounded orifice is occasionally greater than unity owing to the exchange of heat with the surroundings, this exchange voiding the adiabatic assumption.

When it is not feasible to make p_2/p_1 fall below the critical value, the more complicated Eq. (22) must be used. If in addition, the area of the orifice chamber cannot be made 25 times that of the orifice, Eq. (11) must be used.

II. Venturi Meter.

Assuming isothermal flow, and the use of a differential gauge,

$$\frac{u_1^2}{2g} + \frac{BT}{M} ln(p_1/p_2) = \frac{u_2^2}{2g}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For pressure drops small compared with the total (7) can be simplified by expanding[2] the logarithmic term by Maclaurin's theorem as on page 105, giving.

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{\frac{2gBT\,(p_1 - p_2)}{(Mp_2)}} = c\sqrt{2g\,(\Delta h)}. \quad . \quad . \quad (28)$$

The coefficient of discharge has been inserted for the same reasons as given on page 106.

Obviously,

$$u_2/u_1 = p_1A_1/p_2A_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$u_1 = c\sqrt{\frac{2g\,\Delta h}{(p_1A_1/p_2A_2)^2 - 1}}, \quad . \quad . \quad . \quad . \quad (30)$$

$$G = u_2A_2/v_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

$$n = G/M, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

[1] H_2, O_2, N_2, CO and NO.

[2] This simplification leads to the same errors as those shown in footnote on pages 105 to 106.

Where the pressure drops are slight, as in practically all commercial Venturi meters (30) becomes:

$$u_1 = c\sqrt{\frac{2g\ \Delta h}{(A_1/A_2)^2 - 1}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$G = u_2 A_2 / v_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$n = G/M. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34a)$$

III. Pitot Tube.

If an open tube can be inserted into a gas stream with the opening opposite to the direction of flow, there is developed an *impact* pressure in the orifice greater than the static pressure under which the gas exists by an amount corresponding to the kinetic energy possessed by the gas in consequence of its actual velocity. This velocity or dynamic pressure is given by the equation

$$h_i - h_s - \Delta h = \frac{u_{act}^2}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where Δh is the height of a column of fluid of the same density as the gas which exerts this velocity pressure, and is the impact pressure (h_i) minus the static pressure (h_s); u_{act} is the actual velocity approaching the impact opening, and should not be confused with the average velocity, u, of the stream.

$$\Delta h = v(p_1 - p_2) = \frac{BT}{Mp}(p_1 - p_2) = u_{act}^2/2g, \quad . \quad . \quad . \quad (36)$$

$$u_{act} = \sqrt{2gBT\,(p_1 - p_2)/Mp} = \sqrt{2g\Delta h}. \quad . \quad . \quad . \quad . \quad (37)$$

IVa. Flow of Gases through Conduits of Constant Cross-section.

It has been experimentally shown that the flow of gases at room temperature even under high pressure drops through pipes which are too long to be considered orifices, is practically isothermal, and the equations are therefore developed upon this assumption.

The equation of flow for turbulent motion in conduits is based upon the assumptions,[1] that the force of friction is proportional to the surface of contact between fluid and pipe, and approxi-

[1] Eq. (38) has also been derived by physicists from dimensional considerations, and as a result it was shown that f should vary as the dimensionless ratio $du\rho/\mu$.

mately to the square of the velocity; and that friction increases in proportion to the fluid density (ρ).

This force is counterbalanced by the pressure drop which obtains over the entire cross-section of the conduit. Equating these forces, $(\Delta p)(A) = \alpha(\rho)(L)(\text{per.})(u^2)$. The constant of proportionality, α, which may vary with the condition of the inner surface of the pipe, is called $f/2g$, the term $2g$ being put in the denominator to convert the square of the velocity to velocity head, at the same time making the friction factor, f, a ratio. The ratio of cross-sectional area to the perimeter is replaced by the single term "hydraulic radius" (m), so the equation is

$$\Delta p = \frac{(f)\ (\rho)\ (L)\ (u^2)}{(2)\ (g)\ (m)},$$

or expressing the pressure drop in feet,

$$\Delta h = \frac{fLu^2}{2gm}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

This latter form is usually called the *Fanning Equation.* Data concerning the numerical values of the friction factor are given on page 87.

Bernoulli's theorem for turbulent flow through a pipe, therefore, becomes for 1 lb. of gas

$$x_1 + p_1v_1 + \frac{u_1^2}{2g} + \frac{BT}{M} ln\left(\frac{p_1}{p_2}\right) - \frac{fLu^2}{2gm} = x_2 + p_2v_2 + \frac{u_2^2}{2g}. \quad . \quad (39)$$

Assuming that the pipe is sufficiently nearly horizontal that the differences in level may be neglected, and remembering that for isothermal flow $p_1v_1 = bT = p_2v_2$, Eq. (39) becomes:

$$u_1^2/2g + \frac{BT}{M} ln\left(\frac{p_1}{p_2}\right) = \frac{fLu^2}{2gm} + u_2^2/2g. \quad . \quad . \quad . \quad . \quad (40)$$

This expression cannot be applied directly except for slight changes in pressure and correspondingly slight changes in velocity because the friction loss varies with the velocity.

Small Percentage Pressure Drop.—In case the percentage pressure drop is slight and the difference in the squares of the velocity is therefore negligible, remembering as above that the

natural logarithm of p_1/p_2 for this case equals $\frac{p_1-p_2}{p_2}$, Eq. (40) becomes

$$fLu^2/2gm = BT\frac{(p_1-p_2)}{Mp_2} = v_2\,(p_1-p_2) = \Delta h. \quad . \quad . \quad (41)$$

For circular pipes or square conduits, $m = d/4$.

$$\Delta h = \frac{4fLu^2}{2gd} = \frac{2fLu^2}{gd}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

$$Q = Au, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42a)$$

$$G = Q/v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42b)$$

$$n = G/M, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42c)$$

where Δh is the drop in static head caused by the friction loss in the pipe expressed in ft. of gas of the density corresponding to the lower of the two pressures. These equations apply for flow of gases only when the percentage drop in pressure is small, but this is by far the more important case. Values of the coefficient f in these equations are given on page 87.

Large Percentage Pressure Drop.—If the percentage drop in pressure be large the velocity will rise as the pressure decreases and hence a differential length (dL) of pipe must be considered, the differential increase in velocity over the differential length (dL) being (du). The equality of input and output of energy, corrected for friction loss and work of expansion, is

$$u^2/2g + pdv - fu^2dL/2gm = (u+du)^2/2g. \quad . \quad . \quad . \quad (44)$$

Neglecting the second order differentials, this becomes

$$fu^2dL/2gm = -udu/g + pdv, \quad . \quad . \quad . \quad . \quad . \quad (45)$$

Since $u = Gv/A$, $du = Gdv/A$

$$fG^2v^2dL/2gmA^2 = -G^2vdv/gA^2 + bTdv/v, \quad . \quad . \quad (46)$$

or

$$\left[\frac{fG^2}{2gmA^2}\right]dL = -\left(\frac{G^2}{gA^2}\right)\frac{dv}{v} + bTdv/v^3. \quad . \quad . \quad . \quad (47)$$

Integrating [1] (47) between the limits O and L, and v_1 and v_2,

$$fG^2L/2gmA^2 = \frac{G^2}{gA^2}\,ln\,\frac{v_1}{v_2} + \frac{bT}{2}\left(\frac{1}{v_1^2} - \frac{1}{v_2^2}\right). \quad . \quad . \quad (48)$$

Since $p_1v_1 = p_2v_2 = bT$ for isothermal flow (48) may be written

$$fG^2L/2gmA^2 = \frac{G^2}{gA^2}\,ln\left(\frac{p_2}{p_1}\right) + (p_1^2-p_2^2)/2bT. \quad . \quad . \quad (49)$$

Multiplying (49) by $(bT/p_1)^2$ gives

$$\frac{fL}{2gmA^2}\,(GbT/p_1)^2 = \frac{(GbT)^2}{gA^2p_1^2}\,ln\left(\frac{p_2}{p_1}\right) + bT\frac{(p_1^2-p_2^2)}{2p_1^2}, \quad . \quad (50)$$

or

$$Q = GbT/p_1 = Au_1 = A\sqrt{\frac{gBT(p_1^2-p_2^2)/2Mp_1^2}{\left[\frac{fL}{2m} + ln\,\frac{p_1}{p_2}\right]}}. \quad . \quad . \quad (51)$$

For pipes at least 200 diameters in length, the $ln(p_1/p_2)$ may be neglected in comparison with $fL/2m$, and for pipes of any cross-section.

$$u_1 = \sqrt{gmBT(p_1^2-p_2^2)/Mp_1^2fL}, \quad . \quad . \quad . \quad (52a)$$

$$Q = uA, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52b)$$

$$G = Q/v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52c)$$

$$n = G/M. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52d)$$

For pipes at least 200 diameters in length, whose cross-section is circular or square, $m = d/4$, so (52a) becomes

$$u_1 = \sqrt{gdBT(p_1^2-p_2^2)/Mp_1^24fL}. \quad . \quad . \quad . \quad . \quad (53)$$

Or, since $n = u_1A/Mv_1$,

$$n = A\sqrt{gd(p_1^2-p_2^2)/MBT4fL}. \quad . \quad . \quad . \quad . \quad (54)$$

Now $p_1^2-p_2^2 = (p_1+p_2)\,(p_1-p_2)$, and if p_1 be nearly equal to p_2, $p_1+p_2 = 2p_1$. Under such conditions (53) becomes

$$u_1 = \sqrt{gdBT\,(p_1-p_2)/Mp_1 2fL} = \sqrt{\frac{gd\Delta h}{2fL}}, \quad . \quad . \quad . \quad (55)$$

[1] As shown on p. 87, the friction factor for a given gas of constant viscosity in a pipe of constant cross-section varies with the product ($u\rho$). Fortunately this product is constant for gases. In the case of liquids, both u and ρ are constant because liquids are incompressible.

which is identical with (42) derived for these same conditions of low percentage pressure drop in pipes of circular or square cross-section.

It should be noted that equation (42) is based on the assumption that the percentage pressure drop is so small that the difference in the squares of the velocities at the two sections in question are negligible. Eq. (42) gives plus deviations from the correct equation for long pipes (53) as follows: 4 per cent error for 5 per cent pressure drop and 8 per cent for 10 per cent. Since frictional coefficients f are not as accurate as this unless determined on the specific pipe and conditions considered, pressure drops of 10 per cent may be estimated by this simple equation. For larger percentage drops or for pipes shorter than 200 diameters, the more complicated equation (51) should be employed. Eq. (51), while theoretically applicable to all cases of isothermal pressure drop, certainly fails to apply for very short pipes and very high velocity, *i.e.*, when the conditions become comparable to those in orifices, and it must not be used in such cases. This is because the contraction loss at entrance and the enlargement loss at exit were ignored in the derivation.

Eq. (51) is designed for the flow of gases through pipe lines with reasonable pressure gradients, although the drops in pressure in some cases, as for example in the transportation of natural gas or similar products for long distances, may be several times the final pressure. Eq. (51) simplifies to (52) when $fL/2m$ is large compared to $ln\frac{p_1}{p_2}$; little error is made if (52) be used where the length of the pipe is at least 200 diameters. Some writers neglect the logarithmic term for all lengths of pipe, but this is incorrect. Values of the friction factor are given on page 87.

IVb. Flow through Conduits of Constant Cross-section (Viscous Motion).—The equations of flow for straight line motion of gases and vapors in various shaped conduits given in the Summary of Equations (equations 56, 57 and 58) were derived[1] from the definition of absolute viscosity, assuming no motion along the wall.

IV. *Critical Velocity.*—This is derived by equating Δp for turbulent motion and Δp for straight line flow *at the critical velocity.*

[1] See LAMB, "Hydrodynamics," Camb. Univ. Press, 4th Ed. (1916).

For circular pipes, Eq. (38) = Eq. (56), namely

$$(\Delta p_c)=\frac{2\,(f_c)\,(\rho)\,(u_c^2)}{g\,(d)}=\frac{32\mu L u_c}{g(d)^2},$$

whence

$$u_c=\frac{(16)\,(\mu)}{(f_c)\,(\rho)\,(d)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

For annular spaces, Eq. (38) = Eq. (57), namely,

$$\Delta p_c=\frac{f_c\rho L u_c^2}{g(r_2-r_1)}=\frac{8\mu L u_c}{g\left[r_2^2+r_1^2-\frac{(r_2^2-r_1^2)}{ln_e\frac{r_2}{r_1}}\right]}$$

whence

$$u_c=\frac{8\mu(r_2-r_1)}{f_c\rho\left[r_2^2+r_1^2-\frac{(r_2^2-r_1^2)}{ln_e\frac{r_2}{r_1}}\right]}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

For space between drier shelves, Eq. (38) = Eq. (58), namely

$$(\Delta p_c)=\frac{(f_c)\,(\rho)\,(L)\,(u_c^2)}{ga}=\frac{12\mu L u_c}{g(a^2)},$$

whence

$$u_c=\frac{12\mu}{f_c\rho a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

B. DERIVATION OF EQUATIONS FOR WATER

I. *Standard Orifice.*

For isothermal flow

$$x_1+\frac{p_1}{\rho}+\frac{u_1^2}{2g}=x_2+\frac{p_2}{\rho}+\frac{u_2^2}{2g}. \quad . \quad . \quad . \quad . \quad (2b)$$

Inserting the coefficient of discharge, for the same reasons given on p. 106, one obtains for horizontal pipes, or with differential gauge, the same equation as for gases:

$$\sqrt{u_2^2-u_1^2}=c\sqrt{\frac{2g\,(p_1-p_2)}{\rho_2}}=c\sqrt{2g\Delta h}. \quad . \quad . \quad . \quad (19)$$

With large orifice chambers, u_1^2 is negligible compared to u_2^2, so $u_2=c\sqrt{2g\Delta h}$. Both these equations are valid for any percentage pressure drop.

II. *Venturi Meter.*

The derivation is the same as for standard orifice, but the velocity of approach (u_1) is not eliminated from the formula, because it is not customary to attach a large chamber on the upstream side.

III. *Pitot Tube.*

No derivation of equation is necessary. The impact opening measures the static and velocity heads, and by simultaneously determining the static head, the velocity head is obtained by difference which by definition is $u^2_{act}/2g$.

IV. *Flow through Conduits of Constant Cross-section.*

Turbulent Flow.—For isothermal flow

$$x_1+\frac{p_1}{\rho}+\frac{u_1^2}{2g}=x_2+\frac{p_2}{\rho}+\frac{u_2^2}{2g}. \quad . \quad . \quad . \quad . \quad (2c)$$

For constant cross-section, $u_1=u_2$; as developed on pp. 110–111, the friction loss, F, equals $fLu^2/2gm$; for horizontal pipes, $x_1=x_2$. Under such conditions, Eq. (2*b*) becomes the same as that already given for gases.

$$\frac{p_1-p_2}{\rho}=\frac{fLu^2}{2gm}=\Delta h, \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

which is valid for all percentage pressure drops.

Straight Line Flow.—The equations for the straight line flow of water were derived [1] from the definition of absolute viscosity, assuming no motion along the wall.

USE OF MODELS IN STUDYING FLOW OF FLUIDS

It was shown on pages 110 and 111 that the pressure drop through a conduit is of the form, $\Delta p=f\rho Lu^2/2gm$. That discussion involves no assumptions as to the shape or form of the conduit. However, the values of f plotted on page 87 are limited to straight circular pipes, though probably applicable to straight conduits of regular cross section and equivalent hydraulic radius. Where the shape of the conduit is irregular relationships become extremely complicated and not subject to the methods of computation hitherto shown except in an approximate way. However, the principles underlying Fig. 28, as discussed on pages 85 and 86, may be made the basis of a solution of the problem.[1]

The preceding equation may be written, $\Delta p=\phi\rho u^2(L/m,)$ where, as brought out on pages 85 and 86, ϕ is a function of various dimensionless ratios of the variables affecting the case in question, of which Dus/z is usually the most important, where, however, D is, not diameter, but the linear dimension or scale of the equipment. If one wishes to determine the pressure drop which will be encountered in a complicated apparatus, one can make a small model of that apparatus and test the model. If the model is a reproduction to scale of the apparatus, the quantity L/m in the preceding equation is the same for both. If one can determine ϕ, one is immediately in a position to compute the pressure drop through the apparatus. If one will test the model under conditions such that the quantity Dus/z is numerically the same for both the model and the full scale apparatus, ϕ will have the same value in both cases and this value can therefore be determined from the model test. Thus, if one will test the model with the same fluid under the same conditions of temperature and pressure as will be employed in the full scale equipment, the value of s/z is the same in both cases. Hence, it is only necessary to keep the value of Du constant. In other words, if one build a model one tenth full scale, it should be tested with a fluid velocity ten times as great as will be used in the main apparatus. If this requires excessive test velocities, the difficulty may be overcome by using for test denser or less viscous fluids.

The question of the distribution of a fluid flowing through an apparatus is often of vital importance. Distribution may be tested by watching the motion as indicated by threads of smoke introduced into flowing gases or colored solutes into liquids.

This method of testing is of special value in developing drying apparatus (pages 491 to 557), packed tower (pages 576 and 665), sedimentation equipment, furnaces and the like. For purposes of design it is important so to construct the model that the relative shapes and positions of deflecting surfaces can readily be adjusted experimentally to secure the best possible results.

[1] An excellent discussion by A. H. Gibson is found in Engineering, London, Vol. 117, 1924, pp. 325, et seq. The method demands care in analysis of all controlling factors and thorough familiarity with the technique of allowing for their variations.

CHAPTER IV

FLOW OF HEAT

Introduction.—All chemical reactions are accompanied by characteristic and unavoidable heat effects; hence in every problem in chemical engineering design, provision must be made for the satisfactory transference of the heat quantities. Furthermore, even in processes which involve practically no chemical changes, one or more problems of heat transfer usually arise. The laws governing the flow of heat through bodies and from one body to another are therefore of the most far-reaching importance.

The following discussion is restricted to static, uniform conditions of heat flow, *i.e.*, to conditions under which a constant quantity of heat passes each section of path per unit of time, and consequently the temperatures at all points in the system remain unchanged. For a discussion of other cases, see page 187.

For example, in a counter flow air cooler where the air and water flow in opposite directions, the temperature difference between the air and water may be very great at the hot end and very small at the cold end, yet the temperature, and consequently the temperature difference, at any definite point in the apparatus has the same definite value at all times. The above statement not only holds for a counter flow air cooler but also applies to any continuous process after the apparatus has been "tuned up." Even during the tuning-up period temperatures vary so gradually that they may be considered constant over a relatively short period of time. On the other hand, if the temperature of the hot air entering an air cooler vary widely with the time, it is obvious that the temperature at all points in the apparatus would vary with the temperature of the entering air and thus the equations to be discussed below would not be applicable over the entire period of time. But if this period be divided into intervals over which the entering temperature remains practically constant,

the following equations are valid. *In most cases of commercial importance, as soon as the apparatus is tuned up the temperatures at all points in the apparatus do remain essentially constant.*

MECHANISM OF HEAT TRANSMISSION

It is well understood that heat may flow by three mechanisms, which may be defined as follows:

1. *Conduction.*—Heat passing from one part of a body to another part of the same body, or from one body to another in physical contact with it, without appreciable displacement of the particles of the body, is said to flow by conduction.

2. *Convection.*—Convection is the transfer of heat from one place to another within a fluid (gas or liquid) by the mixing of one portion of the fluid with another.

3. *Radiation.*—A hot body gives off heat in the form of radiant energy. When this energy strikes another body, part is reflected. If this second body is transparent or translucent, another part is transmitted. The remainder is absorbed, and quantitatively transformed into heat.[1]

PART I. CONDUCTION

Rarely, if ever, does the question of flow of heat through a *single* homogeneous body arise in engineering practice. In the great majority of cases, heat flows from some medium into and through some solid retaining wall and out into some other medium. The flow through each medium is, therefore, but one step in a more complicated process, and the resistance offered by the retaining wall is only one of a series of resistances. The necessity for a clear insight into the mechanism of this step is obvious, but the ability to apply a knowledge of it to actual problems cannot be attained until the character and significance of each of the other steps involved is studied and appreciated.

(A) FLOW THROUGH HOMOGENEOUS SOLIDS

Newton's Law.—The phenomena of the flow of heat through solid bodies are well understood, and are quantitatively expressed in the form of Newton's law, which states that the quantity of

[1] Except in those relatively rare cases where photo-chemical reactions are induced, or energy is consumed in other special ways.

heat, dQ, passing a given section *at right angles* to the direction of heat flow, is directly proportional to the area of this section, A, to the *difference* in temperature, dt, between the two faces of the section, to the time $d\theta$, and inversely proportional to the thickness, dL. The proportionality constant, k, is known as the coefficient of heat conductivity. Algebraically these relationships are given in the equation,

$$dQ/d\theta = -kA\,dt/dL. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As stated above, this discussion deals only with cases[1] where a constant quantity of heat passes each section of the path per unit of time, so that

$$dQ/d\theta = Q/\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is a constant, and, when given in English units, is expressed as B.t.u. per hr. Thus Eq. (1) becomes for all cases here considered,

$$Q/\theta = -kA\,dt/dL. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the English system, k is expressed as B.t.u. per hr. per sq. ft.[2] of cross-sectional area of path per °F. temperature difference per foot of length of path. This is usually abbreviated to B.t.u. per hr. per sq. ft. per °F per ft. *All data used in the solution of illustrative numerical problems are converted into English units.*

This coefficient of heat conductivity varies greatly for different substances, as shown on pp. 181 to 183. For a given substance, the value of k is apparently a function of the temperature alone. For most cases hitherto investigated this temperature relationship is nearly linear over a considerable range in temperature, that is, $k_t = k_o(1+at)$, k_t being the value at $t°$ F., k_o at 0° F., and a the temperature coefficient.

For example, Nusselt[3] found for burnt infusorial earth (density of 12.5 lbs. per cu. ft.), $k = (0.04)\ (1+0.0014t)$. Hence at 1000° F., k for this material equals $0.04\ (1+0.0014\times1000) = 0.096$. It is to be noted that the temperature coefficient for this insulating material has a positive sign, that is, k increases with the temperature. This holds for the entire class of insulating materials with few exceptions. Figure 45*a* (p. 183), shows the increase in k for insulating bricks with temperature.

[1] However, see p. 187.

[2] In this expression the word *per* is not intended to mean *divided by*, but only to indicate the units involved. The units of k are B.t.u./(ft.)(hrs.)(deg. Fahr.).

[3] *Zeit. Ver. Deut. Ing.*, **52**, 1008 (1908).

On the other hand, the conductivity of good conductors, such as metals, generally decreases with the temperature. Lorenz[1] for lead found $k = 20.5\ (1-0.000471t)$. The notable exceptions to this rule are copper and aluminum.

The variation of k for both insulators and good conductors with the temperature is in most cases so slight that one is justified in using an average value of the heat conductivity as a constant in the integration of the differential Eq. (3) embodying Newton's law.

When the temperature limits are too great to warrant this approximation, the introduction of k as a function of t gives for integration the exact expression for the heat transferred. Available data on conductivities are, however, so approximate that the introduction of a temperature coefficient is in ordinary work a useless refinement unless the particular sample under discussion has been investigated.

The expenditure of time necessary for the integration of Newton's law for many cases frequently met in practice may be avoided by determining its integrated form for certain general conditions. Four such cases will now be discussed, most problems arising in engineering practice falling under the first two cases:

The only variable in these four cases is the area, which will be shown to have certain average values for the several cases.

Case I.—Cross-section of Path Constant. (For Example, Flat Walls and Well-insulated Furnace Electrodes.)

For the flow of heat along any path of constant cross-section, with maintenance of constant temperature at the ends of the path,

$$Q/\theta = -kA\,dt/dL. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Integrating (3) between the limits, L_1, L_2, t_1 and t_2 gives:

$$\frac{Q}{\theta} = \frac{kA(t_1-t_2)}{L_2-L_1} = \frac{kA(\Delta t)}{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In (4), for convenience, the temperature difference, t_1-t_2, has been replaced by Δt, and the thickness L_2-L_1 by L. Eq. (4)

[1] *Wied. Ann.*, **13**; 422, 582; 1881.

states that the rate of flow of heat in B.t.u. per hr.[1] is directly proportional to the coefficient of heat conductivity, k, for the substance in question, to the cross-sectional area of path in square feet, and to the temperature difference in °F between the points from and to which heat is flowing, and is inversely proportional to the length of the path in feet.

Illustration 1.—Calculate the heat loss through a 9-inch brick and mortar wall, 10 ft. high and 6 ft. wide ($k=0.4$) when the inner and outer temperatures are 330° and 130° F., respectively.

Solution.—By Eq. (4),

$$\frac{Q}{\theta}=\frac{(k)\ (A)\ (\Delta t)}{L}=6400 \text{ B.t.u. per hr.}$$

In estimating the heat loss in a proposed installation, the surface temperatures depend on mechanisms other than conduction alone. (See pp. 160 to 170.)

Illustration 2.—Calculate the power loss in kw. due to heat flow *along* a well-insulated graphite electrode (average $k=60$), 6 in. in diameter, the temperature outside the furnace at points 2 ft. apart being 1100 and 250° C.[2]

Solution.—By Eq. (4),

$$\frac{Q}{\theta}=\frac{(k)\ (A)\ (\Delta t)}{(L)}=\frac{(60)\ (\pi/16)\ [(850)\ (1.8)]}{(2)}=9020 \text{ B.t.u. per hr.}$$

This may be converted to kilowatts by the following method, using familiar conversion factors:

B.t.u. per hr.	Ft. lbs. per hr.	Ft. lbs. per min.	hp.	
9020	778	1	1	1
		60	33,000	1.34

$=2.66$ kw.

Equation (4) is the simplest integrated form of Newton's law, and is frequently given as the formal expression of the law itself, rather than the differential Eq. (3), from which it is derived for

[1] Assume for the sake of definiteness, the use of English units. Obviously many systems of units may be and are used. For summary of nomenclature, see pp. 178 to 179.

[2] To convert temperature *difference* from Centigrade to Fahrenheit, multiply by 1.8.

this special case. On account of its simplicity Eq. (4) is usually employed even when the cross-section of path is a variable quantity, average values, A_{av}, for the area A being then employed. The next three cases resolve themselves into the problem of deriving rules for obtaining correct average values for this area.

Case II.—Cross-section of Path Proportional to Linear Dimensions. (Lagged Pipes.)

Where heat is flowing through the sides of a closed cylindrical body of circular section, the direction of flow is at all points radial and perpendicular to the axis, and the cross-section of the path is proportional to the distance from the center of the cylinder. It will now be shown that in such cases the logarithmic mean area should be used.

Consider the flow through a section of thickness dL, see Fig. 33, at a distance L from the center.

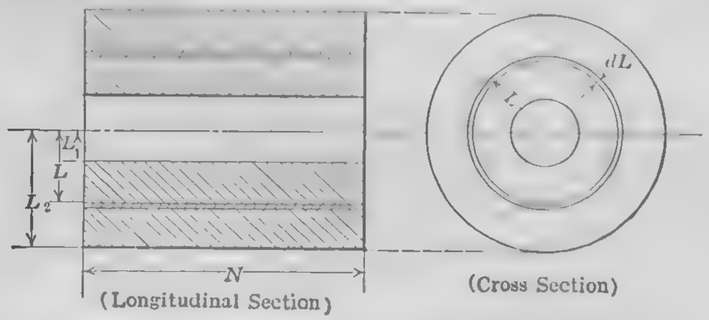


Fig. 33.—Diagram for Case II: Logarithmic Mean Area.

By Eq. (3), $Q/\theta=-kA\ dt/dL$. The cross-section of path is, however, $A=bLN$, where N is the length of the cylinder and b a constant, the value of which depends on its cross-section. ($b=2\pi$ if the section be circular.) This gives

$$\frac{dL}{L}=-\frac{kbN\theta dt}{Q}. \quad \ldots\ldots\ldots \quad (5)$$

On integration and substitution of limits, this becomes,

$$ln_e\left(\frac{L_2}{L_1}\right)=\frac{kbN\theta(t_1-t_2)}{Q}, \quad \ldots\ldots\ldots \quad (6)$$

or, rearranging,

$$\frac{Q}{\theta}=\frac{kbN(t_1-t_2)}{ln_e\left(\frac{L_2}{L_1}\right)}. \quad \ldots\ldots\ldots \quad (7)$$

As stated above, it is desired to use the simple form of Newton's law, Eq. (4), for constant area of path, using, however, an average value of that area A_{av}, which will give the correct heat flow. Equating (7) and (4), one obtains:

$$\frac{Q}{\theta}=\frac{kbN(t_1-t_2)}{ln_e\left(\frac{L_2}{L_1}\right)}=kA_{av}\frac{(t_1-t_2)}{(L_2-L_1)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Whence,

$$A_{av}=\frac{bN(L_2-L_1)}{ln_e\left(\frac{L_2}{L_1}\right)}=\frac{bNL_2-bNL_1}{ln_e\left(\frac{bNL_2}{bNL_1}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$A_{av}=\frac{A_2-A_1}{ln_e\left(\frac{A_2}{A_1}\right)}=\frac{A_2-A_1}{2.3\ log_{10}\left(\frac{A_2}{A_1}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Eq. (10) requires that the average area of cross-section through which the heat is flowing in such a case be computed by dividing the difference of the external and internal areas by the *natural* logarithm of their ratio. The average of two quantities obtained in this way is called their *logarithmic* mean, and is, as will later appear, a value frequently used in problems on the flow of heat. Eq. (9) indicates that A_{av} may also be computed by multiplying the log mean radius by 2π times the length of pipe in feet instead of figuring A_2 and A_1 separately. In the derivation of this rule the assumption has been made that the heat flows radially at every point. As a matter of fact such radial flow will be found only in cylinders of circular cross-section, and for such bodies the rule above given is exact. For sections bounded by smooth curves, the equation is a good approximation—but for rectangular forms other more exact expressions have been determined, which will be given under Case IV. It should be noted that the arithmetical mean of the areas,

$$A_{av}=\frac{A_1+A_2}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

gives a value for the average area checking that of the logarithmic mean within 4 per cent when the value of the expression A_2/A_1 is 2 or less. This accuracy is considered sufficient for all problems in heat flow.

This log mean average area is used chiefly in computations involving heat flow from lagged pipes and insulated wires, when the

outside diameter of the lagging is at least twice that of the pipe.

For the important case of steam pipes lagged with standard magnesia pipe covering, the thickness of covering for high-pressure lines as used in good practice[1] is 2 in. for pipe size up to and including 2-in. nominal diameter iron or steel pipe, $2\frac{1}{2}$ in. of covering for pipe sizes between 2 and 8 in., and 3 in. for sizes above 8-in. pipe. By comparing Eqs. (10) and (11), it is found that the error in using the arithmetic mean instead of the logarithmic mean (10) is greater than 4 per cent only for pipe sizes up to and including 4-in., when covered as above. For sizes above 4-in., therefore, $A_{av}=(A_1+A_2)/2$, with less than 4 per cent error. The *optimum thickness of covering* is that thickness which gives the maximum net saving, *i.e.*, the difference between the value of the heat saved and the total charges against the covering. The literature contains numerous examples of such calculations. See Fig. 34.[2] Obviously the optimum thickness for a given pipe size varies with the value of heat and the cost of lagging the pipe.

Illustration 3.—Calculate the heat loss per 24 hours from 100 lineal feet of standard 1-in. steel pipe carrying steam at 150 lbs. gauge pressure, if the pipe be lagged with 2 in. of a magnesia pipe covering ($k=0.04$ in English units). The temperature just under the canvas is 90° F.

Solution.—A standard pipe of nominal 1 in. diameter has an outside diameter of 1.315 in.[3] As will be shown on p. 170, the temperature of the outer surface of the steel pipe may be taken without appreciable error as that of the steam, or 366° F., which corresponds to steam at 165 lbs. absolute pressure per square inch. The outer diameter of the magnesia is 5.315 in., so the logarithmic mean area per 100 lineal feet is, by Eq. (9),

$$\frac{(100)\frac{(3.14)}{12}(5.315-1.315)}{2.3\ log_{10}(5.315/1.315)}=75 \text{ sq. ft.}$$

NOTE.—The log mean area is used instead of the arithmetic because the ratio of diameters is more than 2 to 1.

By Eq. (4),

$$Q=\frac{(0)\ (k)\ (.1)\ (\Delta t)}{(L)}=119{,}000 \text{ B.t.u.}$$

[1] MARKS, Mech. Eng. Handbook.

[2] MCMILLAN, *Trans. A. S. M. E.*, 37, 961 (1915).

[3] For table of diameters of standard steel pipe, see p. 101

Since the latent heat of condensation of steam at this pressure is 857 B.t.u./lb., the calculated heat loss is equivalent to 119,000/857 = 139 lbs. steam per 24 hours, or

$$\frac{119{,}000}{33{,}500\times 24} = 0.148 \text{ B. Hp. (Boiler Horsepower).}$$

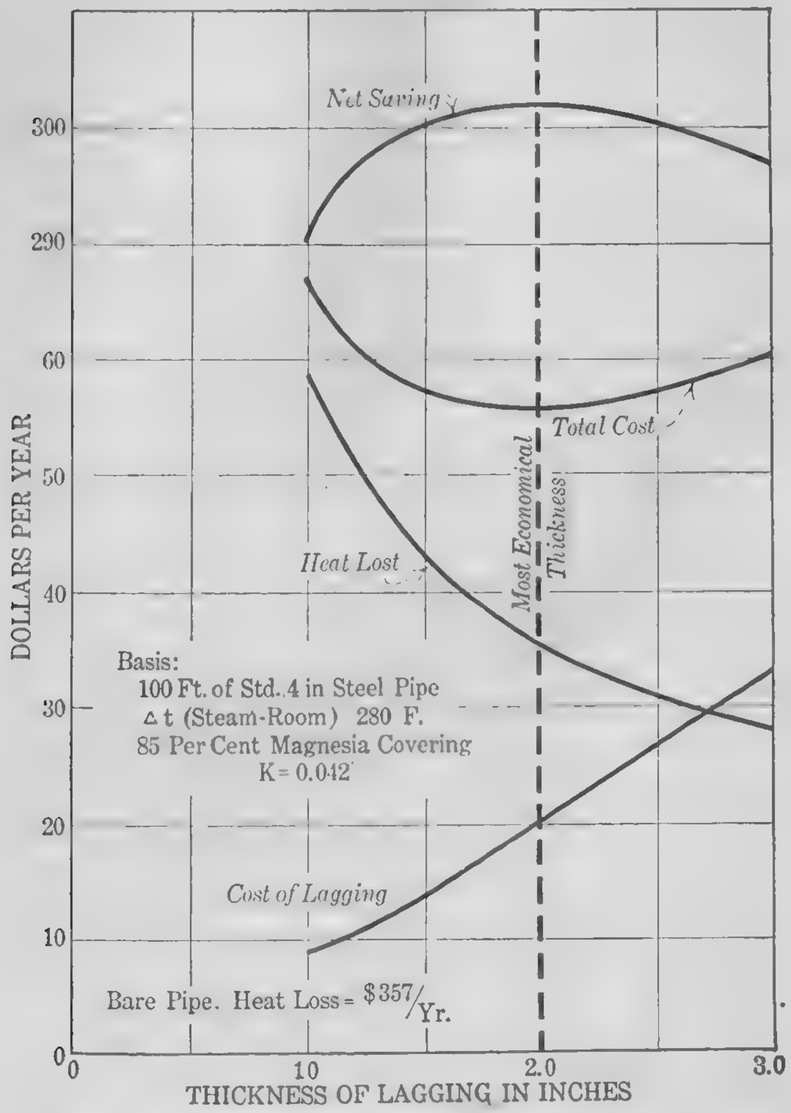


FIG. 34.—Determination of Optimum Thickness of Pipe Covering.

It is possible to have the heat loss from a pipe increased rather than decreased by putting a layer of lagging around it. However, this can occur only under exceptional conditions involving

a combination of poor lagging material with small size of pipe. The maximum loss occurs when the actual outside diameter (d, in ft.) of the insulation is equal to two times the conductivity coefficient of the lagging divided by the total surface coefficient[1] of the lagged pipe, that is,

$$d = \frac{2k}{(h_c + h_r)}. \quad \ldots\ldots\ldots (12)^{2}$$

For example, Fig. 35 shows as ordinates, the calculated heat loss in B.t.u./hr./linear ft. of pipe,[3] having an actual outside

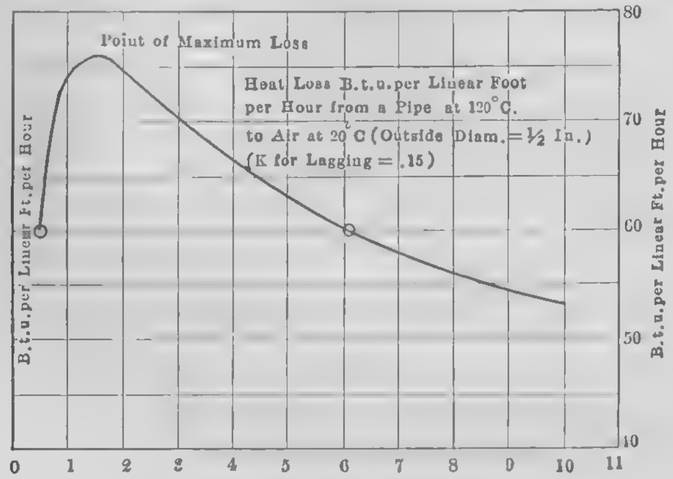

Point of Maximum Loss
Heat Loss B.t.u. per Linear Foot per Hour from a Pipe at 120° C. to Air at 20° C (Outside Diam. = ½ In.) (K for Lagging = .15)
B.t.u. per Linear Ft. per Hour
B.t.u. per Linear Ft. per Hour
50
60
70
80
0 1 2 3 4 5 6 7 8 9 10 11
Outside Diameter of Lagging in Inches

FIG. 35.—Plot Showing Increase in Heat Loss Caused by Lagging a Small Pipe with a Poor Insulator.

diameter of ½ in. against the outside diameter of the lagged pipe in inches as abscissas. This plot shows that the heat loss for such

[1] Values of this coefficient, $h_c + h_r$, are given on p. 169.

[2] This may be shown as follows: In order that the heat loss from the outside area, A_2, of the lagged pipe of radius r feet be a maximum, the total resistance R for the lagged pipe must be a minimum. Now

$$R = \frac{L}{KA_{av}} + \frac{1}{(h_c + h_r)\,(A_2)},$$

$$A_2 = 2\pi Nr, \quad L = r - r_1, \quad \text{and} \quad A_{av} = (\text{Eq. 9}) = \frac{2\pi N(r - r_1)}{\ln \frac{r}{r_1}}.$$

Making these substitutions and placing $dR/dr = 0$, Eq. (12) is obtained.

[3] The pipe temperature is taken as 180° F. above the room.

a pipe lagged with a covering whose conductivity coefficient is 0.15, such as a dense asbestos, actually rises above that of the bare pipe and does not fall to that of the bare pipe until the outside diameter is 6.1 in., which calls for a 2.8 in. thickness of covering. The maximum loss (27 per cent increase over the bare pipe loss) occurs when $d=1.6$ in.

This fact is made use of by the electrical engineer in the insulating of wires to secure a combination of electrical insulation with increased cooling effect on an overloaded wire.

Case III.—Cross-section of Path Proportional to Square of Linear Dimension

Note.—*This case is discussed only for the sake of completeness of presentation; as will appear, the use of the equation derived for this case is unnecessary in any commercial practice hitherto developed.*

Consider the case of any closed solid, through which heat is passing from the interior to the exterior, or the reverse, *radially* in all directions. Such flow is realized only in concentric spheres. If the solid be bounded by concentric spheres of radius L feet,[1] the area through which heat flows is that of a sphere namely,

$$A=bL^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

b being 4π for a sphere. Inserting this value in the general differential equation, Eq. (3),

$$\frac{Q}{\theta}=-\frac{kbL^2dt}{dL}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Integrating between the limits, L_1, t_1, L_2 and t_2, and rearranging,

$$\frac{Q}{\theta}=kbL_1L_2\frac{(t_1-t_2)}{L_2-L_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If now as before, it is desired to calculate the flow of heat on the assumption of an average area, A_{av}, one may equate (15) and (4):

$$\frac{Q}{\theta}=kbL_1L_2\frac{(t_1-t_2)}{(L_2-L_1)}=kA_{av}\frac{(t_1-t_2)}{(L_2-L_1)}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Therefore,

$$A_{av}=bL_1L_2=\sqrt{b^2L_1^2L_2^2}=\sqrt{(bL_1^2)(bL_2^2)} \quad . \quad . \quad . \quad . \quad (17)$$

$$A_{av}=\sqrt{A_1A_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

[1] Assuming, as before for sake of definiteness, English units.

In case, therefore, the cross-sectional area be proportional to the square of the linear dimension, the average area to be employed in calculating the heat flow is the *geometric mean* of the internal and external surfaces, as indicated by Eq. (18). While strictly this applies only to spheres, the equation is an approximation for any closed body whose three dimensions are not widely different.

In the flow of heat through the walls of hollow cubes, such as cubical furnaces, the area of cross-section is proportional to the square of the linear dimension, but all of this area does not receive heat flow *at right angles*. Hence the flow figured on the geometric mean area, $\sqrt{A_1A_2}$, for a cube would be too high. The flow of heat through cubes and the more general case of flow through rectangular bodies having walls relatively thick compared to the inside dimensions, are treated in the next special case.

In the case of beehive coke ovens of commercial size, the geometric mean theoretically applies, but the arithmetic mean is within less than 1 per cent of the geometric. Were the outside diameter twice the inside, the arithmetic mean of the inside and outside areas would be 25 per cent too high, but such cases do not occur in industrial practice. It is to be noted that both the logarithmic and geometric mean values are always lower than the arithmetic.

Case IV. Rectangular Bodies, Having Walls at Least One-half as Thick as the Shortest Inside Dimension

This special case is very important as applied to the loss of heat from electric furnaces, which often have very thick walls. *However, unless the reader is interested in electric furnace design, it should be omitted.*

If the area in Eq. (4),

$$\frac{Q}{\theta}=\frac{k}{L}A_{av}\,(\Delta t),$$

be taken as the inside area, the heat loss so figured will be a great deal too low. On the other hand, if the outer area, or even the sum of the inner and outer areas divided by two (arithmetic mean) be used, the heat loss calculated will be too high. Heat not only flows at right angles to the entire inside area, but it also flows at various angles through the edges and corners of the outside walls. For such cases, the integration of the basic differential Eq. (3), $Q/\theta=kAdt/dL$, becomes difficult, if not impossible. Langmuir[1] has empiri-

[1] Langmuir, Adams and Meikle, *Trans. Amer. Electrochem. Soc.*, **24**, 53 (1913). The form of the equations in this article was determined by a careful analysis of the factors involved, and the coefficients by the device of constructing models of the bodies to be studied or of any symmetrical fractions of those bodies, the interior and exterior surfaces of these models being copper plates, serving as electrodes for a solution of copper sulphate of known concentration and conductivity. The other retaining walls were of glass. The comparison of the conductivity of this cell with one of constant cross-section containing the same solution gave directly the shape factor required.

cally derived [1] the equations given below for an approximate determination of the average area, A_{av}, to be used in the integrated form of Newton's law just given. Consider only bodies bounded by rectangular parallelopipeds, corresponding inner and outer surfaces being parallel, and in all cases the same distance, L, apart. All faces intersect at right angles. There are five special cases given, and it is believed that an understanding of these cases will enable the reader to handle any set of conditions of this type met with in practice.

Case IV*a*.—The Lengths, e, of all Inside Edges are between One-fifth and Twice the Thickness, L, of the Walls

The sum total of the lengths of all the inside edges is Σe. To the actual inside area must be added $0.54L\Sigma e$ to correct for the edges, and $0.15L^2$ for each of the eight corners, this sum being called the average area, A_{av}.

$$A_{av}=A_1+0.54L\Sigma e+1.2L^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Case IV*b*. Length, e, of One Inside Edge is Less than One-fifth the Thickness, L, of Walls

In this case, the lengths of the four inside edges less than $L/5$ are neglected in determining Σe. Then,

$$A_{av}=A_1+0.465L\Sigma e+0.35L^2, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where Σe is the sum total of all the remaining eight inside edges each of which is greater than $L/5$.

Case IV*c*. Lengths of Two Inside Edges are Each Less than One-fifth the Thickness of the Walls

The two short edges are now negligible and the body may be considered as equivalent to a line, of length L, E being the longest dimension of the interior.

$$A_{av}=\frac{2.78EL}{\log_{10}\left(\frac{A_2}{A_1}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Case IV*d*. All Three Interior Dimensions are Less than One-fifth the Thickness of the Walls

Using the same nomenclature,

$$A_{av}=0.79\sqrt{A_1A_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)^2$$

[1] The empirical factors given below closely check those obtained by Langmuir by careful theoretical analyses.

[2] This formula is obviously 21 per cent lower than the ordinary geometric mean area, Eq. (18).

Case IV*e*. When the Walls are Not of Uniform Thickness

Should one encounter a furnace, the various walls of which are not of uniform thickness, the total heat loss should be obtained by adding together the heat loss for each individual wall. That is, A_{av} should be figured for each wall, and then substituted separately in Eq. (4). The edge corrections will thus be figured twice, and the corner corrections three times. Hence for this case, Eq. (19) should read $A_{av}=A_1+0.27L\Sigma e+0.4L^2$, and Eq. (20) should read $A_{av}=A_1+0.233L\Sigma e+0.12L^2$.

The total heat loss for the furnace is, therefore, $\Sigma Q/\theta$, *i.e.*, the sum of the heat losses from the individual walls.

(B) FLUIDS—HEAT FLOW BY CONDUCTION

All conductors of heat, both liquids and gases, follow the same laws as solids, the values of k being, however, very small.[1] At room temperatures, for example, k (B.t.u./hr./sq. ft./°F./ft. thickness) for *stationary* water is 0.35 and for *stationary* air is 0.014, while steel and firebrick in the same units are 25.0 and 0.7, respectively. In both liquids and gases, it is difficult, and under engineering conditions impossible, to eliminate the effect of convection, *i.e.*, the transfer of heat by the movement of the fluid itself, and hence heat transfer in liquids and gases by conduction through the stationary part goes hand in hand with that by convection in the moving parts. This joint effect will be discussed under "surface films" below.

(C) POTENTIAL CONCEPT—CONDUCTION THROUGH SEVERAL SOLIDS IN SERIES

The great majority of transformations of both matter and energy can be conceived as controlled by two factors: one a potential and the other a resistance factor. The total effect produced is in general proportional to the quotient of these two factors. It is obvious that inasmuch as the direction of transformation is controlled by the potential, equilibrium is conditioned upon the potential difference being zero. Since, furthermore, the rate of the transformation is of paramount importance to the engineer, determining as it does the productive capacity of any specific apparatus, *i.e.*, the quantity of production which it is possible to realize in unit time, the fact that the rate is controlled by the potential gives still further importance to this factor.

A familiar application of the potential concept is in the field

[1] For values of k, see pp. 181–183.

of electricity. Electricity does not flow except in the case of a potential difference, the direction of flow is determined by the potential difference, and the rate of flow, *i.e.*, the current is proportional to the potential difference.

Another illustration of a potential is temperature. Heat will not pass from one body to another, or from one point to another, except under the influence of a temperature difference. The direction of flow of heat is determined by the sign of the temperature difference and the rate of flow of heat is proportional to the magnitude of the temperature difference.

Case I. Series Flow

When heat is flowing through each of several bodies in turn, that is, in series flow, it is most convenient to employ the "potential concept." If *electrical resistances* are in series the rate of flow is expressed as amperes (I) or coulombs per second, and this rate is determined by the driving force or voltage difference (Δv), divided by the total series resistance (R) in ohms. $R = r_1 + r_2 + \ldots + r_n$, the sum of the individual series resistances. Further, r is proportional to the length of the path (L) and inversely proportional to the cross-sectional area (A) of the path and inversely to the specific conductivity (k), that is, $r = L/kA$. Thus the familiar electrical equation (Ohm's Law) is

$$I = \frac{\Delta v}{R} = \frac{\Delta v_1 + \Delta v_2 + \ldots + \Delta v_n}{r_1 + r_2 + \ldots + r_n} = \frac{\Delta v}{\frac{L_1}{k_1 A_1} + \frac{L_2}{k_2 A_2} + \ldots + \frac{L_n}{k_n A_n}} = \frac{\text{coulombs}}{\text{seconds}}. \quad \ldots\ldots (23)$$

By analogy in heat flow

$$\frac{Q}{\theta} = \frac{\Delta t}{R} = \frac{\Delta t_1 + \Delta t_2 + \ldots + \Delta t_n}{r_1 + r_2 + \ldots + r_n} = \frac{\Delta t}{\frac{L_1}{k_1 A_1} + \frac{L_2}{k_2 A_2} + \ldots + \frac{L_n}{k_n A_n}} = \frac{\text{B.t.u.}}{\text{hr.}}. \quad \ldots\ldots (24)$$

Thus temperature difference has replaced voltage difference, and B.t.u. per hr. has replaced coulombs per second, but the resistance expression is the same in both cases.

Illustration 4.—A plane section of a furnace wall is made up of 4½ in. of carborundum brick inside ($k = 5.6$), followed by 9 in. of firebrick ($k = 1.0$), and finally 2 in. of mineral wool outside ($k = 0.035$). All values of k are in B.t.u./hr./sq. ft./°F./ft. of thickness. The temperature of the inner surface is 1,100° C., and the outer surface is 200° F.

(*a*) What is the heat loss per hr. per sq. ft. of wall surface?

(*b*) What are the °F. temperatures at each of the double boundaries?

Solution.—Part (*a*).

Basis.—1 sq. ft. of wall:

$$1100°\text{ C.} = (1100)\ (1.8) + 32 = 2012°\text{ F.}$$

Substituting the data in Eq. (24), one obtains:

$$\frac{Q}{\theta} = \frac{2012 - 200}{\frac{4.5/12}{(5.6)\ (1)} + \frac{9/12}{(1.0)\ (1)} + \frac{2/12}{(0.035)\ (1)}} = 325 \text{ B.t.u. per hour.}$$

Solution.—Part (*b*).

Since the heat flows through each of these materials in succession

$$Q/\theta = \Delta t/r_1 = \Delta t/R = 325 \text{ B.t.u. per hour,}$$

whence $\Delta t_1 = (325)\ (r_1) = 22°$ F.

The actual temperature at the boundary between the carborundum and firebrick is then $2012 - 22 = 1990°$ F. Likewise the temperature at the point of contact of the firebrick and mineral wool is 1746° F.

Illustration 4a.—What would be the heat loss in the preceding problem if all walls were circular, the inner wall diameter being three feet?

Solution.—Here the areas of the various materials are unequal. The inside diameter of the carborundum wall is 36 in., and the outside diameter is 45 in. Since the ratio of diameters is less than 2 to 1 the error in using the arithmetic mean in place of the theoretically correct logarithmic mean is very slight, as previously pointed out. If the calculation be based on 1 sq. ft. of outside wall, which has a diameter of 67 in., the average area of carborundum through which heat flows may be taken as $(36 + 4.5)/67$ sq. ft. Similarly the average areas are $(45 + 9)/67$ sq. ft. for the firebrick and $(63 + 2)/67$ sq. ft. for the mineral wool. Substituting in Eq. (24), one obtains

$$Q/\theta = 307 \text{ B.t.u./hr./sq. ft. } \textit{outer} \text{ wall,}$$

or 570 B.t.u. per hr. per sq. ft. of *inner* wall.

Case II. Parallel Flow

In electrical flow with the individual resistances in parallel, the same voltage difference causes current to flow through each resistance as if it alone were present. In such cases, it is custom-

ary to calculate the flow by adding the reciprocals of the resistances, and multiply this sum by the voltage difference.

$$I=\left(\frac{1}{r_1}+\frac{1}{r_2}\right)(\Delta v). \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

In heat flow an analogous equation is used in connection with the simplified radiation equation (see p. 167).

(D) FLOW FROM SOLID TO SOLID

When heat passes through a surface from one solid to another it is probable that at the boundary no temperature drop is found, as assumed in the preceding numerical examples. This, however, requires perfect contact between the solids, and the absence of gases or vacant spaces caused by those blow holes, bubbles, rough surfaces, etc., which are very likely to be present where two solids are brought together. Even traces of poorly conducting material between metals, such as oxide films on the surface, will cause abrupt drops in the temperature. It is usually impossible to estimate the thickness of such films, but their effect may be serious. In order to allow for the conductivity of the mortar bond in brick walls, for example, an experimental wall is generally made up in the laboratory and the heat loss determined. The resulting conductivity of the type of brick in question thus includes the conductivity of the mortar.

PART II. CONVECTION

Film Concept.—When a liquid or gas is in contact with a solid there is strong evidence to show the presence of an adhering relatively stationary film of fluid on the surface of the solid, a film which becomes thinner as the velocity of the fluid parallel to the surface increases, but which breaks away from the solid only at very high velocities, if at all. Through such a film, heat can be transmitted by *conduction* only, although once the heat has penetrated the film the hot molecules are picked up and carried away *mechanically* by the swirling motion of the main body of the fluid, *i.e.*, the transfer is mainly a matter of *convection*, and in the latter case the resistance to flow will be negligible. Since most liquids and gases are exceedingly poor conductors of heat, it is not surprising to find a large resistance to heat flow at the boundary

surface of a fluid and solid (and also at the boundary between a liquid and a gas), accompanied by a large drop in temperature at this point.[1] The temperature change in the neighborhood of a solid-fluid boundary is indicated in Fig. 36. Through the solid there is a fall, t_2-t_3, which is usually small compared to the temperature drop in the boundary itself. Through the surface film the drop t_3-t_4 is very great, but once the zone of the stationary fluid is passed the temperature soon reaches that of the main portion of the fluid, t_5. No attempt has been made to draw Fig. 36 to scale.

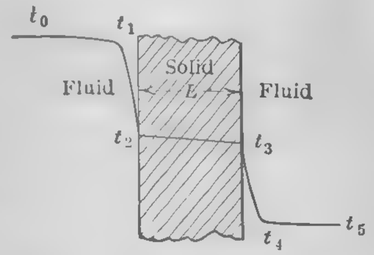


FIG. 36.—Diagram Illustrating Film Concept.

In treating this exceedingly important case of heat transfer, the assumption is made that the surface film of the fluid is of a definite though unknown thickness, and that therefore the quantity of heat transmitted per unit time can be expressed by the equation:

$$\frac{Q}{\theta}=hA\,(t_3-t_5)=hA\Delta t, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where the coefficient, h, replaces the term k/L in Eq. (4), k being the coefficient of conductivity of the fluid, and L the *unknown thickness* of the surface film. This coefficient h is often called the "film coefficient," or "surface coefficient." In English units, h is expressed as B.t.u./hr./sq. ft./°F. temperature difference. In contra-distinction to k—the "coefficient of conductivity" previously discussed—*the "surface" coefficient, h, contains no elements of thickness.*

From what has been said of the mechanism of the transmission, it is not surprising that this important coefficient, h, is by no means constant, even for a given fluid, but is a complex function of a number of variables such as the physical properties of the fluid, the nature and shape of the solid surface, and the velocity of the fluid past the solid boundary. In many important cases the variation of this coefficient with the conditions is a thing at present impossible to estimate except semi-quantitatively. This,

[1] See also pp. 37 to 39.

combined with the fact that the resistance to heat flow through such boundaries is frequently the largest and the controlling factor in cases of heat transfer, renders the problem one of the most serious the engineer must face. In all attempts to reduce the boundary resistance between fluid and solid, experience has proven that the most effective means are those tending to reduce the thickness of the surface film. Thus a rapid movement of the body of the liquid or gas past the surface can greatly decrease the resistance by tearing off the film. In the important special case of heat transmission into a boiling liquid, the formation and disengagement of bubbles on the heating surface, as well as the convection currents in the liquid mass both so greatly aid in the diminution and rupture of the surface film that it is possible to find surface coefficients into a boiling liquid six-fold those into the same liquid below its boiling point. On the other hand, if the temperature difference between the surface and the boiling mass be slight, it is possible to form a more or less continuous film of vapor on the heating surface, the disengagement of which is very slow, and which acts as an insulating layer between the solid and liquid. Under these conditions the coefficient can be very low, but will rise rapidly with increasing temperature difference and the consequent stirring produced by the rapid evolution of the bubbles.

The following equation expressed in terms of the potential concept for series flow applies to the important case of two fluid films separated by a solid retaining wall.

$$\frac{Q}{\theta}=\frac{\Delta t}{\frac{1}{h_1A_1}+\frac{L}{k_2A_2}+\frac{1}{h_3A_3}}=\frac{\Delta t}{R}=HA_{av}\Delta t. \quad . \quad (27)$$

$$HA_{av}=\frac{1}{\frac{1}{h_1A_1}+\frac{L_2}{k_2A_2}+\frac{1}{h_3A_3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where H is the *overall* coefficient of heat transfer from the hotter to the colder fluid. The average area (A_{av}) on which this coefficient is based may be taken as any one of the three individual areas involved; for the sake of definiteness the basis should be stated.

For flat walls, or where the difference in the areas of the two films and the plate may be neglected, Eq. (27) becomes:

$$\frac{Q}{\theta}=\frac{A\Delta t}{\frac{1}{h_1}+\frac{L_2}{k_2}+\frac{1}{h_3}}=HA\ (\Delta t).. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Overall versus Film Coefficients.—Consider the case where steam is condensing at constant pressure on the outer surface of a pipe and cooling water is flowing through the pipe at a definite velocity. Each of the three resistances will have a definite value under these conditions, thus fixing the value of the overall coefficient H. Now if the water velocity be doubled, the thickness of the film of water on the tube wall will be decreased. Experimentally, it is found that this thickness is not quite halved, and hence h_3 is not quite doubled; in general, the coefficient h_3 between the pipe and the cooling water varies directly as some power, n, of velocity. Now the other two resistances will remain practically unchanged, so if an attempt be made to express H as a function of the water velocity, it will result in the introduction of this variable to a power other than the true value of n. The literature furnishes numerous examples of such cases, and while the equation proposed by such writers would give the correct result if all the experimental conditions were reproduced, they furnish little information to one interested in the numerical value of H for a case in which the mechanism is identical, and yet where a different combination of fluids and kinds of retaining wall is involved. Furthermore, it is true that such writers have neglected to include one or more very important variables in their equations (such as viscosity), with the result that variables used in their equations for H must also take care of fluctuations in the variables omitted. Since viscosity varies quite rapidly with temperature, this last situation makes it practically impossible to duplicate the results of such experimenters even when working with the same fluids and retaining walls, unless one is within the same range of temperature that prevailed in the experimental work. *The logical and by far the simplest method is the development and tabulation of equations for the various film coefficients.* With reliable data of this sort available, the designer can calculate the film coefficients for the case of interest to him and combine and use them by means of Eq. (27). When it is realized that nine or more

variables affect the overall coefficient H in the important case of the transfer of heat in condensers, it is seen that it is practically hopeless to get an accurate expression for H, unless one adopts the simplification of calculating the special value of H for the particular case in hand from equations involving h_1 and h_3, each of which is determined by a number of variables fewer than those which determine H. The truth of this statement will be illustrated by the use of equations given below. It is felt that the lack of progress in the development of equations for the prediction of heat transfer coefficients is due primarily to the prevailing custom of ignoring the resistance concept, and the failure to utilize suitable "mental pictures" concerning the various resistances involved.

The various film coefficients will be taken up in the following order:

A. Liquid Films, Liquid Not Boiling (Warming and Cooling).

(1) Natural Convection.
(2) Forced Convection.
  (*a*) Inside Pipes.
  (*b*) Outside Pipes.

B. Liquid Films, Liquid Boiling (Evaporation and Distillation).

C. Gas Films (Warming and Cooling).

(1) Natural Convection.
(2) Forced Convection.
  (*a*) Inside Pipes.
  (*b*) Outside Pipes.

D. Condensing Vapors (Condensers).

All data for film coefficients h will be given as B.t.u. per hr. per °F. temperature drop through the film per sq. ft. film surface. Equations, data, and nomenclature are summarized on pp. 175 to 185. Mean temperature difference is discussed on pages 171 to 174.

A. Liquid Films, Liquid Not Boiling.

(1) *Natural Convection.*—In the absence of propulsion of the liquid past the heating surface by external force, the only motion of the liquid is due to *natural convection, i.e.*, the mechanical convection currents set up due to the difference in density of the liquid at various points. The rate of circulation varies widely

with the shape of the vessel, viscosity of the liquid, and temperature difference. As the warming proceeds, both temperature difference and viscosity of the liquid decrease; since these variables have opposite effects, the film coefficient tends to remain fairly constant during the warming period. For *water*, with free channels for natural convection, average values of h from 50 to 300 are realized. For very viscous liquids, with poor arrangements for convection, values as low as from 10 to 20 are possible. The value of H for any desired combination obviously depends on the number and type of series resistances.

Stose and Whittemore,[1] working upon the preheating of sugar and molasses solutions of various viscosities and densities, have derived the following empirical equation for natural convection for their apparatus:

$$h = 50\sqrt[3]{J\Delta t}, \quad \ldots\ldots\ldots \quad (30)$$

covering a range of values of h from 60 to 260. In their experiments Δt, the drop in temperature through the liquid film, varied from 60 to 130° F., and J, the fluidity[2] of the solution relative to water at 68° F., varied from 0.05 to 1.6. The heating was accomplished by a $\frac{3}{8}$-in. copper steam coil immersed in a 10-gal. tank containing a 12-in. depth of liquid, the temperature of the outer surface of the pipe being measured directly by means of thermocouples.

(2*a*) *Forced Convection Inside Pipes.*—As a result of a critical survey[3] of the literature and an application of "dimensional considerations," it has been found that the film coefficient[4] depends upon the thermal conductivity of the liquid k, the inside

[1] Undergraduate thesis, Chemical Engineering, M. I. T., 1922.

[2] For a more detailed discussion of viscosity and its reciprocal, fluidity, see pp. 79–85.

[3] McAdams and Frost, *Refrigerating Engineering*, **10**, No. 9 (March, 1924).

[4] The film coefficient is calculated by dividing the observed rate of heat flow per square foot of film surface by the observed drop in temperature through the film. The latter was obtained by deducting the drop in temperature through the wall of the pipe from the observed drop from the outer surface of the pipe to the liquid flowing through the pipe, the skin temperature of the outer wall of the pipe being measured by thermocouples. The film temperature was obtained by subtracting from the temperature of the inner wall, one-half of the mean temperature difference between the inner wall of the pipe and the main body of the liquid flowing inside the pipe.

diameter of the pipe D, and the ratio of length to inside diameter r, and is a function of a group of variables called the "modulus." This modulus (Dv/z) depends on three factors, namely, mass velocity v of liquid (pounds per section per square foot of cross-section), diameter D of the pipe in inches, and average viscosity z of the *film* of liquid on the inner wall of the pipe. The Frost equation for the turbulent flow of *water* inside smooth pipes is as follows:

$$\frac{hD}{k}=14.5\left(1+\frac{50}{r}\right)\left(\frac{Dv}{z}\right)^{0.8} \quad \ldots\ldots\ldots (31)$$

and is based on $k=0.35$ for water. Equation 31 is plotted on Fig. 37 as the line CD. In the bulk of the data used in determining the constant of Eq. 31, the value of r was 100; hence in this case

$$h=\frac{207}{D^{0.2}}\left(\frac{u}{z}\right)^{0.8} \quad \ldots\ldots\ldots (32)$$

By very careful cleaning of the pipe one obtains values of h higher than given by Eq. 32. If the pipe be fouled with scale, slime, or other deposit, as is often the case, one should allow for the thermal resistance of the scale, employing the resistance concept (pp. 131–138). Orrok[1] found considerable difference in testing new and old Admiralty-metal condenser tubes.

For the scale on the old tube, one finds[2] that $k/L=1920$, and this value was independent of the water velocity. Since the water-side resistance and hence the overall resistance varies with water velocity, it is unsound to allow for scale by multiplying the overall coefficient by a cleanliness factor. The resistance of the deposit should therefore be estimated from the thermal conductivity of the deposit and the probable thickness of the foreign material.

When data for *air* are plotted on Fig. 37, one obtains the line EF for turbulent flow and the lines LE and ME for very low velocities.[3] The meager data for light lubricating oils of low viscosity give the line BA for turbulent flow and GA for viscous motion.[4] If the data for turbulent flow of all fluids fell on a

[1] *Trans. A. S. M. E.*, **32** (1910).

[2] McAdams, Sherwood, and Turner, *Trans. A. S. M. E.*, **48** (1926).

[3] The lines LE and ME are based on the data of Nusselt and Jossie respectively. While this discrepancy exists, fortunately such low velocites, are of no commercial importance; the economical velocities for gases fall in the range EF.

[4] The lines BA and GA intersect at an abscissa of 14 whereas the lower critical velocity for isothermal flow corresponds to $DV/z=9$ (see pp. 73 to 87).

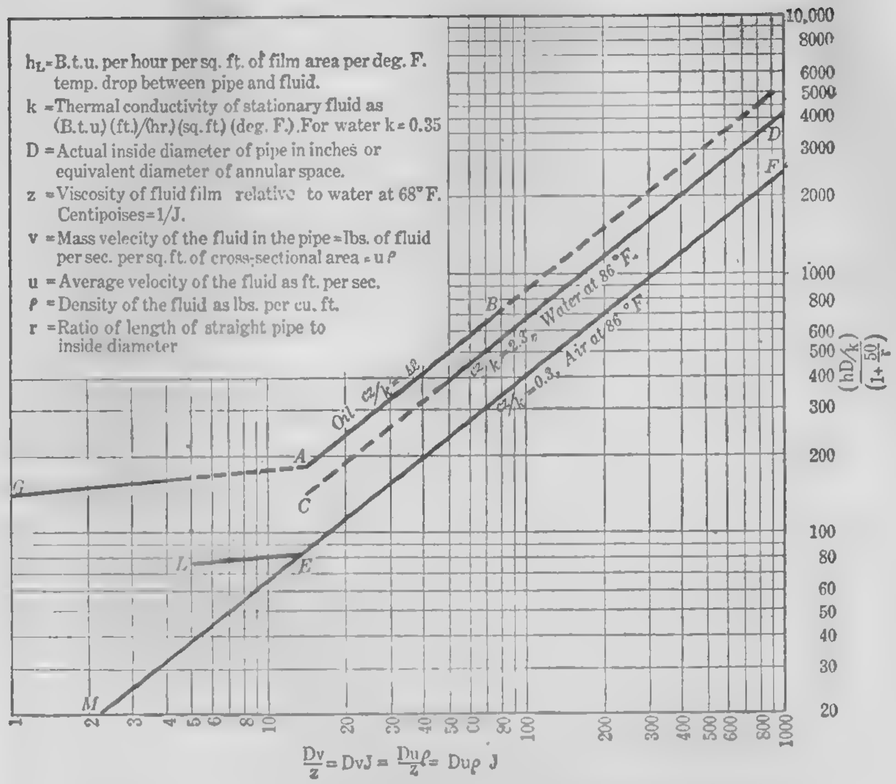

h_L = B.t.u. per hour per sq. ft. of film area per deg. F. temp. drop between pipe and fluid.
k = Thermal conductivity of stationary fluid as (B.t.u) (ft.)/(hr.) (sq. ft.) (deg. F.). For water k = 0.35
D = Actual inside diameter of pipe in inches or equivalent diameter of annular space.
z = Viscosity of fluid film relative to water at 68°F. Centipoises = 1/J.
v = Mass velocity of the fluid in the pipe = lbs. of fluid per sec. per sq. ft. of cross-sectional area = u ρ
u = Average velocity of the fluid as ft. per sec.
ρ = Density of the fluid as lbs. per cu. ft.
r = Ratio of length of straight pipe to inside diameter
Oil, z/k = 18
z/k = 2.3, Water at 86°F.
z/k = 0.3, Air at 85°F.
A
B
C
D
E
F
G
L
M
$\frac{Dv}{z}=DvJ=\frac{Du\rho}{z}=Du\rho J$
$\frac{(hD/k)}{(1+\frac{50}{r})}$

FIG. 37.[1]—Film Coefficients for Fluids Flowing Inside Pipes.

[1] When heating oils in the range G-A, an increase in average temperature difference from pipe to oil has a marked effect in increasing h. This may be explained as follows. In isothermal flow, *i.e.*, when the temperature difference is zero, true viscous motion exists, and the fluid velocity has no radial component, hence the film extends to the axis of the pipe, see Chapter II. But when the fluid is being heated, the temperature of the fluid near the wall is higher than in the central core, setting up a viscosity gradient. As a result of the decreased viscosity near the wall, the fluid velocity at this section increases, requiring a decrease in velocity of the fluid nearer the axis of the pipe. The development of the radial components of the fluid velocity sets up convection currents, thereby increasing h.

single curve on Fig. 37, this would mean that the only variables influencing heat transfer are diameter, velocity, viscosity, conductivity of the fluid, and the ratio of length to diameter. It seems certain that other variables play a part, particularly the specific heat c of the fluid. It is not improbable that the different results obtained with the several fluids are due primarily to differences in specific heat which, however, must appear in some other dimensionless ratio, such as cz/k. In other words, the differences in location of the lines for these fluids are probably due

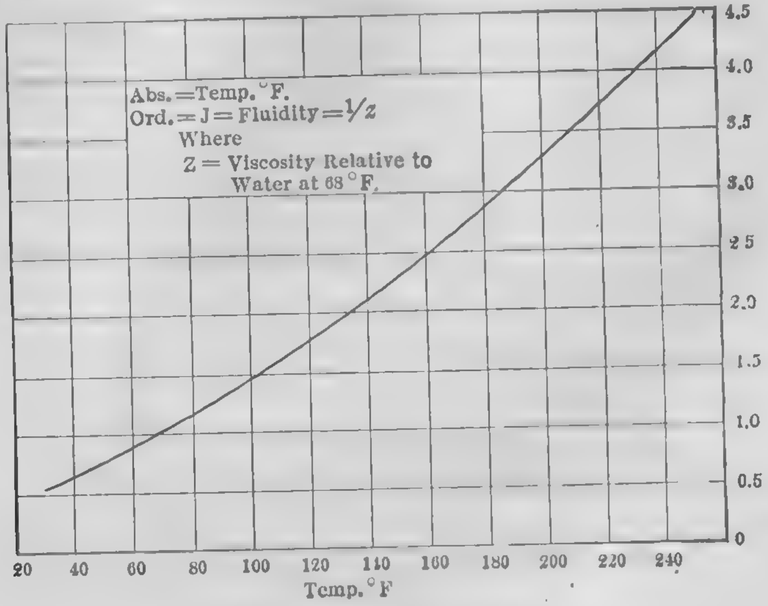


FIG. 38.—Fluidity of Water.

to the differences in cz/k, this variable being equivalent to another axis in the diagram. It has been suggested that this correction factor is a power function[1] of cz/k. An exponent of 0.25 will correlate the data for air and water, but the best data available for oil falls somewhat lower than would be called for by this exponent. The lines drawn represent the best experimental data now available for these fluids. If one is dealing with materials of intermediate values of cz/k, it is recommended that one interpolate between these curves. For gases the Dixon equation is convenient, see page 149.

[1] McADAMS and FROST, *Ind. Eng. Chem.*, **14**, No. 1 (January, 1922) 12; C. W. RICE, *Ibid.*, **16**, No. 5 (May, 1921), 454.

Inspection of Fig. 38 shows why the film coefficient of heat transfer for liquid flowing in turbulent motion inside pipes increases with rise in temperature. (For information concerning the fluidity and viscosity of various liquids, and the conversion of viscosity units, see pp. 79 to 85.)

For oils, both K and J are less; for the very heavy oils J is only a small fraction of that of water. For this reason, the film coefficient for *oil, especially when cold*, may be quite small compared to that for water.

Illustration 5.—An "oil to oil" heat interchanger in a continuous solvent-recovery plant is to operate as follows: 100 gal. per minute of hot paraffin oil at 250° F. enter the inner pipe of a standard 1¼-in. by 2-in. "double-pipe condenser" (made of steel) and leave at 120° F.; 105.3 gal. per minute of "rich" oil containing 5 per cent gasoline enter the annular space at 70° F., flowing in a direction opposite to the warmer oil. To simplify the illustration, assume that the 2-in. pipe is lagged so that heat losses to the surroundings may be neglected. In order that the friction drop be not greater than the available pressure, the oil velocity in the inner pipe must not exceed 4 ft. per second. Calculate the total linear feet of double pipe required, specifying arrangement of same.

Data.—The inner and outer dimensions of 1¼-in. standard pipe are 1.38 and 1.66 in., and for 2-in. standard pipe are 2.07 and 2.38 in. The standard length of such pipe is 18½ ft. The specific heat of the pure oil and the oil-gasoline solution is 0.5, and the specific gravity of both oils is 0.91. The cross-section of inner pipe is 0.0104 sq. ft., the sectional area of the annular space is 0.00833 sq. ft., and k for steel pipe is 25.0. There are 7.48 U. S. gal. per cubic foot and 8.33 lb. water per U. S. gallon. The thermal conductivity of both hot oil and the mixture may be taken as 0.082. The following table gives the viscosity z, in centipoises.

Temperature, degrees Fahrenheit....	120	140	160	180
Viscosity of lean oil.....	2.00	1.66	1.42	1.25
Viscosity of rich oil.....	1.80	1.50	1.28	1.13

Solution.—Each 1¼-in. pipe will handle (0.0104) (4) (60) (7.48) = 18.7 g.p.m. (gallons per minute). To handle 100 g.p.m., therefore, there must be (100/18.7) or six double pipes in parallel. Therefore, the actual linear velocity in the 1¼-in. pipe is 100/(6) (60) (7.48) (0.0104) = 3.57 ft. per sec., and 4.69 ft. per second in the annular space.

In order to determine the length of pipe theoretically needed, the heat-transmitting surface must be figured by Eq. (27). The rich oil will rise (250 − 120)/1.053 = 123° F., leaving at 193° F. The temperature difference from oil to oil is 250 − 193 = 57° F. at the hot end and 120 − 70 = 50° F. at the cold end, and hence the overall temperature difference, Δt, for the whole

process averages 53.5° F. The heat to be transferred is that given up by the hot oil, or

$Q/\theta = (100)(60)(8.33)(0.91)(0.5)(250-120) = 2{,}960{,}000$ B.t.u. per hour.

To estimate the film temperatures, assume that say two-thirds of the overall temperature drop of 53.5° F. occurs through the inner film. Taking this drop as 34°, and that through the outer film as 18°, leaves 1.5° for the wall itself. The mean temperature of the oil in the annular space is $(70+193)/2 = 131.5°$; hence the outer film temperature is $131.5+(18/2)$ or about 141° F., and the mean temperature of the inner film is $185 - (34/2) = 168°$ F. From a plot of the viscosity data, the corresponding viscosities are found to be 1.48 for the rich oil outside, and 1.35 for the lean oil inside.

For the *inner* oil film, $DV/z = (1.38)(3.57)(62.3)(0.91)/1.35 = 207$; $cz/k = 0.5\ (1.35)/0.082 = 8.23$. By interpolation from Fig. 37 the corresponding ordinate is $1{,}350 = \dfrac{\frac{hD}{k}}{1+\frac{50}{r}}$.

Since $r = 18.5\ (12)/1.38 = 161$, $1+\frac{50}{r} = 1.31$; hence $h\ (1.38)/0.082 = 1{,}350\ (1.31) = 1{,}770$, whence $h = 105$.

For the *outer* film, the equivalent diameter is 0.41 in., as shown on page 145. Then $DV/z = 0.41\ \ (4.69)(62.3)(0.91)/1.48 = 73.7$, and $cz/k = 0.5\ (1.48)/0.082 = 9.0$ and the corresponding ordinate from Fig. 37 is 600. Here $r = 18.5\ (12)/0.41 = 542$, and $1+\frac{50}{r} = 1.09$; hence $hD/k = 654 = h\ (0.41/0.082)$, whence $h = 131$.

k/L for the steel $= 25(12)/0.14 = 2140$. Let N be the total lineal feet of double pipe. The total resistance may now be calculated from Eq. 27 (p. 136).

$$R = r_1 + r_2 + r_3 = \frac{1}{(105)\ (1.38)\ (3.14)\ (N/12)} + \frac{1}{2{,}140(1.52)\ (3.14)\ (N/12)} +$$

$$\frac{1}{131(1.66)\ (3.14)\ (N/12)} = \frac{0.0453}{N} = \frac{\Delta t}{Q/\theta} = \frac{53.5}{2{,}960{,}000};$$

whence $N = 2{,}510$ lin. ft.[1]

Since this is to be divided into six parallel banks of pipe, each bank would contain 418 ft. of double pipe, or 23 lengths each 18.5 ft. long.

Any heating surface installed in addition to that calculated, to provide a "factor of safety," should be placed in series with the above, for if it were placed in parallel, the resulting decrease in velocity and coefficient of heat transfer would almost entirely offset the intended factor of safety. For this case, a factor of safety of 50 per cent is recommended; *i.e.*, the calculated length should be multiplied by 1.5.

[1] The value of r_1/R is $0.0266/0.0453 = 0.588$, hence the drop through the inner film is $0.588\ (53.5) = 31.4°$, *versus* 34° assumed. This slight discrepancy introduces an error well within the precision of the data; hence it is unnecessary to revise the trial temperatures employed.

(2*b*) *Forced Convection Outside Pipes.*—Little experimental data are available for the flow of liquids in annular space between concentric pipes so widely used in heat interchangers. For the present, it is suggested that Fig. 37 be used for this case, employing for the value of D that diameter having the same "hydraulic radius" as the annular space involved. The hydraulic radius of a circular pipe is one-fourth the inside diameter, while for such an annular space it is one-half the clearance. Use of this suggestion is made in the problem last preceding.

B. Liquid Films, Liquid Boiling

Little data are available on the values of h_B between a metal and a boiling liquid. However, overall values, H (including the surface coefficient of a condensing steam film, the conductivity of a metal, and the boiling liquid film) are available. The principal factors which seem to influence the value of H are temperature difference between metal and liquid, viscosity and density of the liquid, arrangement of the heating surface, and the *cleanliness*[1] of the heating surface, *i.e.*, whether covered with crystals, scale, etc. A large number of tests[2] on six different commercial types of evaporators in sugar factories gave values of H (from condensing steam to boiling sugar solution) ranging from 130 to 510, varying with conditions.

In an evaporator or still the substitution of a tube material of greater conductivity and less thickness for a steel tube or pipe is never followed by a proportionate increase in the capacity of the apparatus, as illustrated by the following example.

Illustration 6.—A solution is boiling in an open pan and is heated by exhaust steam; the heating surface consists of 1 in. standard steel pipe of 0.133 in.wall having a conductivity coefficient of 25 B.t.u. per hr. per sq. ft. per °F. per ft. of thickness. It is proposed to replace the steel pipe by copper tubing having the same outside diameter (1.315 in.), walls 0.040 in. thick, and a conductivity coefficient of 220 B.t.u./hr./sq. ft./°F./ft. thickness. Since the conductivity of copper is about nine times that of steel and its thickness one-third as great, if tube material were the controlling factor, a twenty-nine fold capacity would be anticipated.

If the overall coefficient H, from steam to boiling solution be 300 B.t.u./hr./°F./sq. ft. of outer area when steel pipe is used, what percentage increase in capacity can in fact be expected if copper be substituted for the steel?

[1] Pridgeon and Badger, *Ind. Eng. Chem.*, 16 (May, 1924), 468; McCabe and Robinson, *Ibid.*, 472.

[2] Kerr, *Trans. A. S. M. E.*, **38**, 67 (1916).

Solution.—Basis: 1 sq. ft. of outer wall.

The inside areas in square feet are 0.797 for the steel and 0.940 for the copper and the mean tube areas in sq. ft. are 0.898 for the steel and 0.970 for the copper. The value of 2000 B.t.u./hr./sq. ft. film area/°F. will be used for the surface coefficient of the steam film in both cases.

Equating the sum of the series resistances to the overall resistance,

$$1/(2000)\ (0.797)+0.133/(12)\ (25)\ (0.898)+1/h\ (1)=1/300\ (1),$$

whence $h=452$ for the boiling film outside the pipe. This same film will be present outside the pipe when the tube material is changed so the total resistance using copper instead of steel will be

$$1/(2000)\ (0.94)+0.04/(12\ (200)\ (0.97)+1/(452)\ (1)=1/363$$

when copper tubes are used. Since the overall drop in temperature from steam to boiling liquid, Δt, is the same in both cases, the rate of heat flow and consequently the capacity will be inversely proportional to the total resistances. Hence the capacity using copper tubes will be 21 per cent greater than when steel pipes were used.

In *enameled apparatus* with low-pressure steam condensing outside a cast-iron or steel wall enameled on the inner surface, and with water boiling inside, the overall coefficient H in some cases is about 200. As a rule, enameled apparatus will not stand pressure much above 50 pounds steam gauge which is equivalent to a temperature of 298° F. in the jacket, and obviously the temperature of the liquid in the apparatus will be much lower. Where higher temperatures are desired, hot oil is circulated through the jacket. Where the oil velocity is low the overall coefficient from oil to liquid may be only 10 to 20.

Although the data concerning the film coefficient h_B from metal to boiling liquid are meagre, it is believed that in the case of water it may vary from 200 to 4000.

C. Gas Films.

(1) *Natural Convection.*—Gas film resistances to heat flow are of a much greater order of magnitude than those offered by liquid films.

The surface coefficient h of a gas film depends on its thickness and the conductivity of the gas, which in turn depend on the gas film temperature. If the only gas currents tending to thin down this film are due to natural causes, the convection is said to be "natural." An illustration of such a case is found where a steam pipe is losing heat to the air in a room. As previously stated, the heat flows *through* the film by conduction, and is carried away

from the film by convection.[1] The coefficient for such a case is often called the "convection coefficient." In the following discussion this coefficient will be referred to as h_a. The value of h_a depends upon a number of factors, such as the position, shape, condition and magnitude of the surface, upon the density of the gas, upon the temperature of the gas film, and upon the temperature difference between the surface of the solid and the main body of the gas. All known solids when exposed to a cooler gas lose heat, not only by convection to the gas, but also by radiation to the surroundings. When the radiating power of the solid is known, the convection loss, and therefore, the convection coefficient h_a can be calculated by difference. Unfortunately, as will be discussed below, the radiating powers of most solids are not accurately known, and consequently there are little reliable data available for h_a. Langmuir[2] in order to minimize the radiation correction in his experiments for the determination of convection coefficients, chose silver as the solid, since it radiates less heat than any other available material. The results of Langmuir's experiments on a 6-in. silver disc with one side exposed to air in a room may be closely expressed by the equation:

$$h_a(\text{from a vertical surface})=0.28(\Delta t)^{0.25}, \quad \ldots \ldots (33)$$

where Δt, the °F. temperature difference between the surface of the plate and the main body of air in the room, varied from 10 to 850. Using the same silver disc, Langmuir[3] found h_a to be about 10 per cent greater on the upper side and 50 per cent less on the lower side of the horizontal disc, than when it was in a vertical position.

Considering other data available, the following equation is recommended for an *estimation* of the convection coefficient for *vertical walls*, of commercial size.

[1] Heat is also lost in this case by the separate mechanism of radiation, see pp. 160 to 170.

[2] *Trans. Am. Electrochem. Soc.*, **23**, 299 (1913).

[3] Loc. cit. Taking into account the variation of the conductivity of the gas film with the temperature, Langmuir found that his experimental heat loss could be predicted by assuming a constant thickness of 0.4 cm. of stationary air film on the silver surface. This held between 150 and 500° C. Only a small proportion of the total heat loss from the silver surface was by radiation; it was found that the hand must be brought within approximately 0.4 cm. of the silver surface before marked increase in temperature could be noted. This demonstrates the existence of the air film, see pp. 36 to 39.

$$h_a = 0.7 + \frac{\Delta t}{375}, \quad \ldots\ldots\ldots (34)$$

where Δt varies between 10 and 400° F. temperature difference between the wall *surface* and the air in the room. It is true that certain fibrous substances permit the formation of a somewhat thicker surface film than is found on smooth walls, but the coefficient is probably independent of the material proper except as this influences the surface condition.

The convection loss from horizontal steam pipes to air, for either bare or lagged pipe, can be estimated by Eq. (34), but for pipes smaller than 5 in. the value should be increased and for larger pipes it should be decreased. When figuring h_a for lagged pipe, care should be taken to employ for Δt the °F. temperature difference between the *surface* of the lagging and the air, not between the steam pipe and air.

Numerical problems will be found under "simplified radiation formula," pp. 167 to 170. This is because the convection loss is always accompanied by a radiation loss.

(2*a*) *Forced Convection; Gas Flowing Inside Pipes.*—When air is caused to flow past a solid, for example, by a fan, higher values of h_a result as the film is made thinner. Such convection is called "forced." A knowledge of the value of the coefficient of heat transfer between a gas and a solid by conduction plus convection under any chosen conditions is essential in the design of steam boilers, feed water heaters installed in boiler stacks, superheaters, gas coolers, gas heaters, and other types of apparatus, depending on forced gas circulation. Because of its importance, much experimental work has been done in determining h_a for this case of gases flowing *inside* pipes of circular section under special conditions chosen by the various experimenters[1] because their work was often being done for industrial concerns. These and others have suggested various equations to represent the results, some of them extremely complex and unwieldy. The equation derived by each of these holds within the experimental error for the particular conditions maintained during the individual test but is inapplicable to conditions widely different from

[1] Wm. Nusselt, *Vercin Deutsche Ing.*, **89** (1910); Fessenden and Haney, *Univ. of Mo. Bull.*, vol. 17, No. 26 (1916); Babcock and Wilcox, 35th Ed. of "Steam," 328 (1913), and 1916) "Experiments," published in pamphlet form; H. P. Jordan, *Proc. Inst. Mech. Eng.* (1909).

the experimental ones. Dixon[1] considered all the data obtained by the above investigators and offers the following equation, which is general for all gases investigated. It correlates the reliable data and is recommended as the best equation so far developed for turbulent[2] flow inside pipes or in annular spaces between concentric pipes.

$$h_a = 0.22\ C_p T_f^{3/5}\ v^{0.8}/D^{0.2}, \quad \ldots\ldots\ldots (35)$$

where v[1] is in pounds of gas per second per square foot of free area; C_p is the average specific heat at constant pressure; T_f is the mean temperature of the gas film, expressed in degrees Fahrenheit absolute; and D is the equivalent diameter of the gas passage, in inches. Equation (35) is substantiated by experimental data of various investigators for equivalent diameters from 0.3 to 4 in., for mean film temperatures from 626 to 1650° R., for velocities from 0.2 to 30 lb. of gas per second per square foot of free area, and is based on data for illuminating gas, air, and carbon dioxide. This mass velocity[3] is equal to the average linear velocity (feet per second) through the clear area multiplied by the density (pounds per cubic foot) of the gas at the temperature and pressure in question, *i.e.*,

$$v = u\rho, \quad \ldots\ldots\ldots\ldots (36)$$

For ordinary calculations with air inside 1-in. pipes, approximately the correct coefficient is given by the equation:

$$h_a = f v^{0.8}, \quad \ldots\ldots\ldots (35a)$$

where f depends on the film temperature. When the latter is 200° F., $f = 4$. This expression should not be used with very small tubes or very high temperatures, where the general equation (36) must be employed.

Illustration 7.—Gases from a sulphur burner (18 per cent SO_2, 2.9 per cent O_2, 79.1 per cent N_2) at 1600 °F. are to be cooled to 75° F., by passing inside lead pipe (4-in. inside diameter and ¼-in. wall) immersed horizontally

[1] W. T. Dixon and W. H. McAdams, article in preparation.

[2] See pp. 87 and 141. Equation (35) does not apply to viscous flow.

[3] Reynolds (*Phil. Trans.*, 1883) was the first to point out the advantage of expressing gas velocity as a mass rather than a linear velocity. All equations of value proposed in the last 10 years employ this mass-velocity concept.

in a wooden tank through which cooling water is circulated. Each pipe is connected by a return bend to the pipe directly below it, and the top and bottom rows have a horizontal header for introducing the gases at the top and removing them from the bottom of the cooler. Cooling water enters the bottom of the tank at 70° F. and overflows at the top at 180° F. In order to handle 20,000 cu. ft. of gases (measured at 75° F. and 1 atm. absolute pressure) per hour, (*a*) how much cooling water is required? (*b*) how many linear feet of pipe are necessary if the linear gas velocity leaving the cooler be not over 15 ft. per sec. in each 4-in. pipe?

Solution.—Part (*a*) The molal heat capacities[1] of the gases concerned are as follows:

$$MCp\ (SO_2) = 7.0 + 0.0071T - 0.00000186T^2,$$

$$MCp\ (O_2,\ N_2) = 6.5 + 0.001T,$$

where T = the instantaneous °C. absolute temperature. The total heats to be removed from each of the component gases in one mol of the mixture from the burner, could be calculated by integrating these equations between the limits of $T_1 = (460+1600)/1.8 = 1143°$ C. absolute and $T_2 = 297°$ C. absolute, but are more conveniently read from the total heat curves given in Fig. 5, p. 14. Thus the net heat given up by 1 lb. mol of SO_2 in cooling from 1600 to 75° F., is 17,100 − 380 = 16,720 B.t.u., while for 1 lb. mol. of O_2 or N_2, the net heat given up is 11,000 B.t.u. The total mols of burner gas to be cooled per hour are

$$\frac{(460+32)\ (20{,}000)}{(460+75)\ (359)} = 51.2 \text{ lb. mols per hour.}$$

$$Q/\theta = (51.2)\ (0.18)\ (16{,}720) + (51.2)\ (0.791+0.029)\ (11{,}000)$$

$$= 615{,}000 \text{ B.t.u. per hour.}$$

Since the water has a specific heat of 1.0 and rises 110° F. in passing through the jacket, the necessary water

$$= 615{,}000/(60)\ (110)\ (1)\ (8.33) = 11.2 \text{ G. P. M. (gallons per minute).}$$

Solution.—Part (*b*) The initial temperature difference between gases and water is 1420° F., the final is 5° F., and the mean, as will be shown on p. 185, is

$$\frac{\Delta t_1 - \Delta t_2}{2.3\ log_{10}\left(\frac{\Delta t_1}{\Delta t_2}\right)} = 251° \text{ F.} \quad \ldots\ldots\ldots \quad (52)$$

Since the cross-sectional area of a pipe whose inside diameter is 4.00 in is 0.0873 sq. ft., the number of pipes in parallel to handle all the gas at an exit velocity of 15 ft. per sec. would be 20,000/(15) (3600) (0.0873) = 4.24. Hence 5 pipes must be used, thus making the actual exit velocity 12.72 ft. per sec. in each 4 in. pipe.

The average molecular weight (M) of the gas is

$$(0.18)\ (M \text{ for } SO_2) + 0.791\ (M \text{ for } N_2) + 0.029\ (M \text{ for } O_2) = 34.6.$$

[1] G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **34**, 1128 (1912).

The mass velocity of the gas through the pipes will be

$$v = \frac{(u)\ (492)\ (M)}{(460+t)\ (359)} = 1.127 \text{ lbs.}$$

gas per sec. per sq. ft. of cross-sectional area.

The value of h_G from gas to pipe is given by Dixon's equation, Eq. (35):

$$h_G = \frac{0.22 C_p T_f^{3/4} V^{0.8}}{D^{0.2}}$$

The values for the symbols in Eq. (35) are calculated as follows:

$$log_{10}\ v^{0.8} = 0.8\ log_{10}\ 1.127 = 0.0410, \text{ so } v^{0.8} = 1.10,$$

$$log_{10}\ D^{0.2} = 0.2\ log_{10}\ 4 = 0.1204, \text{ so } D^{0.2} = 1.32.$$

$$C_p = \frac{\text{B.t.u. removed}}{(\text{°F. fall in temp.})\ (\text{lbs. gas})} = \frac{0.227 \text{ B.t.u. per lb.}}{\text{°F.}},$$

Neglecting the drop in temperature through the pipe wall and water film, the gas film temperature is calculated by adding one-half the mean temperature drop through the gas film to the mean temperature of the water. Hence,

$$T_f = 460 + \frac{70+180}{2} + \frac{251}{2} = 1170°\text{R.};\ T_f^{2/3} = 111$$

Substituting these values in Eq. (35), $h_G = 4.62$.

Now h_L for the moving water outside the pipes will be more than 200, so this resistance is less than 1/200, and may be neglected in series with 1/4.62. Likewise the resistance of the pipe L/K, or 1/960, may be neglected in comparison to 1/4.62. So the gas film can be considered as the total resistance and

$$A = \frac{Q/\theta}{h_G(\Delta t)} = \frac{615{,}000}{(4.62)\ (251)} = 530 \text{ sq. ft. of inside area.}$$

Since each linear foot has 1.045 sq. ft. inside area, the total length of pipe required is 507 linear feet of 4-in. pipe.

Since there are to be five pipes in parallel, the length of each parallel row must be 102 ft. Each of the five parallel rows should consist of sufficient length to provide its cooling surface (102 linear feet) plus enough additional length to allow for the flanges and return bends, which would be placed outside the wooden tank which forms the jacket. In order to allow for the deposition of sulphur in the pipes, a *factor of safety* of 2 is suggested, *i.e.*, the apparatus should consist of five parallel banks of pipes, each bank containing say 200 linear feet of pipe, exclusive of bends.

(2*b*) *Forced Convection—Gas Flowing at Right Angles to Pipes.*—For gas flowing outside pipes, data for air only are available.

Based on the data of King, Kennelly, and Hughes, Chappell[1] derived the following equation for air flowing at right-angles to *single* pipes:

$$h_G = 0.8 T_f^{1/3}\ v^n / D^{0.53}, \quad \ldots\ldots\ldots \quad (37)$$

[1] E. L. Chappell and W. H. McAdams, *Trans. A. S. M. E.*, **48** (1926).

where $n=0.60+0.08 \log_{10} D$. T_f is the average film temperature in degrees Rankine, v represents the pounds of gas per second per square foot of free area, and D is the outside diameter of the pipe in inches. The overall range of the various factors is as follows: T_f from 595 to 1,410, v from 0.04 to 11, D from 0.001 to 2, and h_G from 3.5 to 410. At low velocities one should calculate the value of h_c for free convection (see p. 147), employing the higher of the two coefficients, h_c and h_G. Also, radiation must be separately calculated (see pp. 160–171).

For air flowing at right angles to *staggered* pipes, a comparison of Eq. 37 with the data of Carrier, Sturtevant, Reiher, and others, showed that the equation should be modified as follows:

$$h_G=\frac{0.8T_f^{1/3}w^n}{D^{0.53}}\left(1+\frac{D}{W}\right) \quad \ldots\ldots\ldots \quad (38)$$

where W is the distance in inches, between the centers of adjacent pipes in a row taken at right angles to the direction of air flow, and w represents the pounds of air per second per square foot of *minimum* free area between the pipes in a plane at right angles to the air flow. The correction term for staggering, $1+\frac{D}{W}$, applies only when the pipes are arranged substantially equilaterally.

For gases other than air, it is suggested that h_G from Eqs. 37 and 38 be multiplied by the ratio of the specific heats of the gas and of air, both taken at the average gas temperature.

The Buffalo type of hot-blast heater used by Carrier was constructed from standard 1-in. wrought-iron pipes. The center-to-center distance of pipes in the same row was $2\frac{5}{8}$ in., the distance between center lines of adjacent rows was $1\frac{7}{8}$ in., and the minimum free area through the first row was roughly 50 per cent of the frontal area. For these conditions the Carrier equation[1] is as follows:

$$h_G=22.3w/(1.42+w), \quad \ldots\ldots\ldots \quad (39)$$

where w varied from 0.25 to 1.5 lb. per second per square foot of minimum free area. In comparing tests on various air heaters, Carrier found that any standard construction which increases air friction increases h_G.

[1] W. H. Carrier, *Trans. A. S. M. E.*, **33** (1911).

Illustration 8.—1000 cu. ft. of air per minute (measured at 20° C.) is to be heated from 20 to 100° C. by being blown outside and perpendicular to standard 1-in. steel steam pipes, the center line of the pipes being spaced on equilateral triangles so that there is 1 in. clear space between the pipe surfaces. The superficial air velocity is 10 ft. per sec. at 20° C. How many linear feet of pipe will be required when the steam pressure is 20 lbs. gauge?

Note.—Sp. ht. of air = 0.241; barometer is normal.

Solution.—Eq. (39), applies to such conditions, which represent good engineering practice. The superficial velocity is that which would exist were the pipes not present. The outside diameter of 1 in. pipe is 1.315 in., so in every 2.315 in. there is 1 in. clear space, or 43 per cent clear area. Thus, the actual velocity through the *minimum* clear area is

$$u=(10)\ (2.315)/1=23.2 \text{ ft. per sec. at } 20° \text{ C.}$$

The volume of a molecular weight of any permanent gas at standard conditions (S. C.) *i.e.*, 32° F., and sea level pressure, is 359 cu. ft. The molecular weight, M, of air is 29. The Centigrade temperatures must have 273 added to convert them to absolute temperature, and the volume of a gas varies directly as its absolute temperature. The pressure (p) is taken as normal barometric, namely, 14.7 lbs. per sq. in.

The mass velocity required for Eq. (39) is

$$w=(u)\ \frac{(273)\ (M)\ (p)}{(273+t)\ (359)\ (14.7)}=1.74 \text{ lbs. air per sec. per sq. ft. free area at the } \textit{minimum} \text{ cross-section.}$$

By Eq. (39),

$$h_G=\frac{22.3w}{1.42+w}=12.3 \text{ B.t.u./hr./sq. ft. heating surface per °F.}$$

	Cu. ft. per min.	Cu. ft. per hr.	Cu. ft. per hr. at S.C.	Lb. mols per hr.	Lbs. per hr.			
$\frac{Q}{\theta}=$	1000	60	273 / 293	1 / 359	29	0.241	(100-20)	1.8

$=157{,}000$ B.t.u. per hr.

The temperature of the steam corresponding to 35 lbs. absolute pressure per sq. in. is 126° C., so the difference between steam and air is 126 − 20 = 106° C. at the cold end and 126 − 100 = 26° C. at the hot end. As will be shown on p. 185 the mean temperature difference for such a case is given by Eq. (52):

$$\Delta t_{av}=\frac{\Delta t_1-\Delta t_2}{2.3\ _{10}log\left(\frac{\Delta t_1}{\Delta t_2}\right)}=\frac{106-26}{2.3\ log\left(\frac{106}{26}\right)}=57° \text{ C.}$$

or (57) (1.8) = about 103° F.

As will be shown on page 170, there is no appreciable temperature drop through the condensing steam film or through the metal pipe,

$$A = \frac{Q/\theta}{(h_G)\Delta t} = \frac{157{,}000}{(12.3)\ (103)} = 124 \text{ sq. ft.}$$

Since 2.91 linear feet of standard 1-in. pipe are required to give one square foot of outside area, the total length necessary is 361 linear feet of standard 1-in. steel pipe.

D. Condensing Vapor Films

When a vapor is in contact with a solid, the temperature of which is lower than the condensing temperature of the vapor under the pressure in the container, the vapor will condense upon the surface of the solid, and in so doing will give up at constant temperature its heat of condensation (equal to the heat of vaporization), a quantity that is always large. Unless the container be so narrow that throttling can occur, the condensation will take place at constant temperature, as otherwise pressure differences would be developed on the various parts of the condensing surface, differences which it is of course impossible to maintain if there is the possibility of free movement of the vapor from point to point.

For the condensation of vapors containing air only to the extent of that dissolved in the original liquid, considerable data are available for the condensation of *steam* on the outer surface of pipes. Webster [1] found values for steam ranging from about 1440 to 3240, the coefficients increasing as the arithmetic average steam velocity varied from 1 to 7 lbs. per sec. per sq. ft. At a given velocity increasing the absolute pressure from 18 to 90 lbs. per sq. in. seemed to decrease the coefficient somewhat.

Jordan [2] obtained similar results for steam but his coefficients at a given steam velocity and pressure were considerably lower than those found by Webster. Clement and Garland [3] found coefficients for steam varying from 1470 to 2410. More recent data [4] for steam at atmospheric pressure give coefficients varying from 2060 to 3360. Since the quantitative effects of the various variables which effect the coefficient on the steam side have not been determined, the value of 2000 is suggested for ordinary

[1] *Trans. Inst. Engrs. and Shipblds. in Scotland*, vol. **57** (1913–14).
[2] *Engineering* (London), 1909.
[3] Univ. of Ill., Eng. Expt. Sta. *Bull.* 40, 1909.
[4] McAdams and Frost, *J. Ind. Eng. Chem.*, vol. **14**, No. 1 (1922).

calculations. This assumes, however, the presence of non-condensable gas in small amounts only, and provision for the rapid and efficient removal of condensate from the heating surface and non-condensable gas from the condenser, *i.e.*, conditions representing good engineering practice. Although the actual value of h_v will vary considerably from case to case, fortunately the coefficient on the steam side is not usually the controlling factor in the case of condensers, evaporators and stills. In the case of preheaters for air or other gases the resistance on the gas side is usually so high that the resistance on the steam side is negligible in comparison.

In the case of vapors other than steam much lower coefficients are found. This is because the coefficient is determined by the conductivity and fluidity of the *condensate*.

This point is illustrated by the following table:[1]

	(h_v)	(J)	(K)	$\left(\frac{h_v}{JK}\right)$
Steam	2,190	3.05	0.329	2,180
	3,360	3.86	0.329	2,650
	2,475	3.16	0.329	2,380
Carbon tetra-chloride	283	1.85	0.0610	2 510
Benzene (C_6H_6)	306	2.81	0.0806	1 350
	366	2.87	0.0806	1 580

Thus the greater part of the ratio of about 8-fold in the coefficients for steam and organic vapors is explained by the lower values of the thermal conductivity (K) and fluidity (J) of the organic condensate. Additional experiments should be made to determine the effects of other variables, such as vapor velocity. In the absence of experimental data for vapors other than those quoted, the following equation may be used as an approximation.

$$h_v = 2{,}200KJ. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

The addition of non-condensable gas to condensing steam has a marked effect in lowering the film coefficient h_v from vapor to metal. Fortunately, in good engineering practice it is possible to keep the percentage of non-condensable gas small, even in

[1] *Ibid.*

multiple effect evaporation, where steam is condensing under vacuum. This is also possible in the case of steam-heated rolls used for the drying of paper, cloth, etc., but the practice in this field is not as well standardized as it should be. Fig. 39 shows how the coefficient h_v[1] varies with the arithmetic mean percentage of air in steam. It will be noted that the curves by the different investigators do not check; this is due to the fact that the coefficient is not plotted against the proper variable, or group of variables, as the case may be. C. S. Robinson gives the following equation:[2]

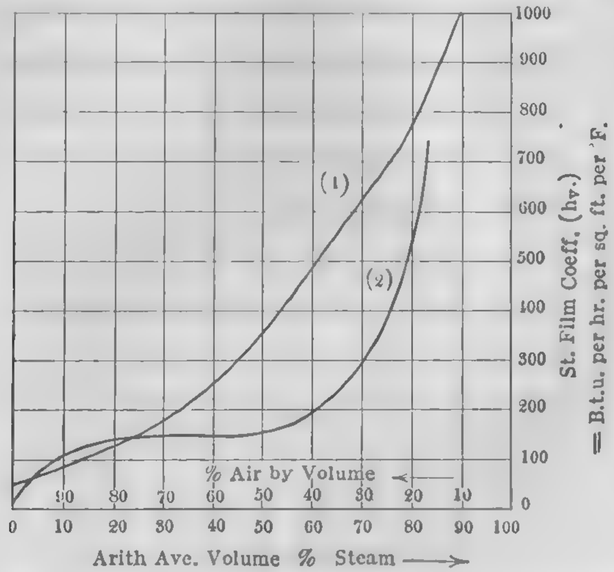


FIG. 39.[1]—Effect of Air on Film Coefficient from Condensing Steam to Pipe.
(1) Recalculated data of Chambers and Eskew.
(2) Arzoomanian and Alpert.

$$\log_{10} h_v = 1 + 0.0246 \text{ (per cent steam by volume)}.$$

Equations for the overall coefficient from steam to cooling water in surface condensers have been suggested previously by Smith, Orrok and others. The average value of H for a number of installations of surface condensers is given by the latter as 350.[3]

[1] Data of CHAMBERS and ESKEW, M. I. T. Chem. Eng. Thesis, 1921, as recalculated by T. H. FROST, M. I. T.; data of ARZOOMANIAN and ALPERT, M. I. T. Chem. Eng. Thesis, 1922.

[2] Based on Kerr's overall coefficients from condensing steam to boiling sugar solutions; see *J. Ind. Eng. Chem.*, **12** (1920), 644.

[3] ORROK, *Trans. A. S. M. E.*, **32** (1910).

Calculation of H by the resistance method is desirable, though in many cases the major resistance in a surface condenser handling steam is on the water side,[1] especially where low water velocities are used. When condensing organic vapors, the resistance on the vapor side becomes higher than in the case of steam.

Illustration 9.—A condenser is to handle 1500 lbs. per hour of dry, saturated alcohol vapor at normal barometric pressure and cool the condensate to 75° F. operating with cooling water which passes up through standard ¼-in. seamless drawn copper tubes. The alcohol vapor enters at the top and passes down around the tubes and the water enters the tubes at the bottom at 60° F. and leaves at the top at 120° F. with a linear velocity of 2 ft. per sec. How many tubes must be installed, and what must be the length of each?

Data.—The specific heat of alcohol is 0.65 B.t.u./lb./°F., the heat of vaporization is 372 B.t.u./lb., and the boiling point is 173° F. The inside and outside diameters of the ¼-in. copper tubing are 0.375 and 0.540 in. and the conductivity coefficient of the copper is 220 B.t.u./hr./sq. ft./°F./ft.

Solution.—Two operations are performed in this "condenser"; the condensation of alcohol vapor at a constant temperature of 173° F., and the cooling of the condensate from 173 to 75° F. The coefficient of heat transfer has different values in each of these two stages.

The heat removed in condensation is (1500) (372) = 558,000 B.t.u./hr., while for cooling it is (1500) (0.65) (173 − 75) = 95,500 B.t.u./hr. Since the water flows first through the cooling and then the condensing zone, the temperature rise in the cooling zone must be $\frac{95{,}500}{558{,}000+95{,}500}$ or 14.6 per cent of the total rise of 60° F., or approximately 9° F. Hence the cooling water at the end of cooling and the beginning of condensation is 69° F. The temperature difference between condensing vapor and water is 173 − 120 = 53° F. where the water leaves the condensing stage, and 173 − 69 = 104° F. as it enters. The arithmetic mean or 78.6° F., may be taken with less than 4 per cent error, as stated on p. 174. For the cooling stage, the temperature differences at the ends are 104° and 15° F., so the log mean temperature difference must be used, which gives by Eq. (52),

$$\frac{104-15}{2.3 \log\left(\frac{104}{15}\right)} = 46° \text{ F.}$$

Since the water has a specific heat of 1.0 and a temperature rise of 60° F., the necessary water for this condenser is

$$(558{,}000+96{,}000)/(60)\ (60)\ (8.33) = 21.8 \text{ G. P. M. (gallons per minute).}$$

The cross-section of each tube is 0.000766 sq. ft., and since the linear water velocity in each tube is to be 2 ft. per sec., the number of tubes must be 31.7

[1] See also p. 140.

or 32 tubes. This water velocity gives a conductance coefficient h_L of 526 according to Eq. (32).

Since the value of K for alcohol is 0.1025 (see p. 182) and the average value of J is 2.22 (see Fig. 26, p. 83), the surface coefficient for the condensing vapor film h_v found by Eq. (40) to be 501, then Q/θ for the condensing stage is, by Eq. (27),

$$\frac{78.6}{\frac{1}{(526)(N)(3.14)(0.375/12)}+\frac{0.0825/12}{(220)(N)(3.14)(0.458/12)}+\frac{1}{(501)(N)(3.14)(0.540/12)}}$$

$=558{,}000$, whence $N=240$ linear feet for condensation.

The average temperature difference in the cooling stage is 46° F., Q/θ is 95,500 B.t.u./hr., and assuming the coefficient h_3 between the outside of the tube and the condensed alcohol as 50, $N=334$ ft.

The total feet of pipe required is 240+334 or 574 linear feet, and if there are 32 tubes in parallel, the length of each will be 18 ft.

Optimum Velocity (Economic Balance).—In the above equations it will be noted that velocity is an important variable and one largely within the control of the designer. Thus, in air heaters for ventilating systems, driers, humidifiers, etc., one may use a high air velocity, thereby securing a high coefficient of heat transfer, but this is done at the expense of a high pressure drop. If desired, one may go to the other extreme and use a very low air velocity requiring therefor a large heating surface but involving very little pressure drop and therefore only small power consumption. As pointed out by Carrier and Busey [1] in connection with the design of hot blast heaters, the decision as to the velocity to be employed in the given case requires an economic balance between cost of power and cost of heating surface. The curves [2] in Fig. 40 have been calculated for the heating of 10,000 cu. ft. per min. from 70 to 170° F., using steam condensing at 220° F. in a heater made of staggered standard 1-in. pipe. The coefficients were figured from the Carrier [3] formula and the pressure drops from the Sturtevant [4] tables. The cost of heating surface was taken as $0.927 per sq. ft. including all installation costs. The combined (overall) efficiency of fan and motor was assumed to be 50 per cent and the cost of power 3 cts. per kw.-hr. The

[1] *Trans. A. S. H. V. E.*, **19**, 141 (1913).
[2] LEWIS, MCADAMS, and FROST, *Jour. A. S. H. V. E.*, **28**, 104 (1922).
[3] See p. 152.
[4] See p. 89.

drier for which this apparatus was designed operates 7200 hr. per year, *i.e.*, 300 days. The charge against the heating surface for depreciation, interest, taxes, maintenance, etc., was assumed to be 15 per cent.

It will be noted that the point of lowest total cost corresponds to an initial air velocity of about 10 ft. per sec. through the minimum clear area. The reason for this is that whereas the charges against heating surface are annual, the power cost necessary to

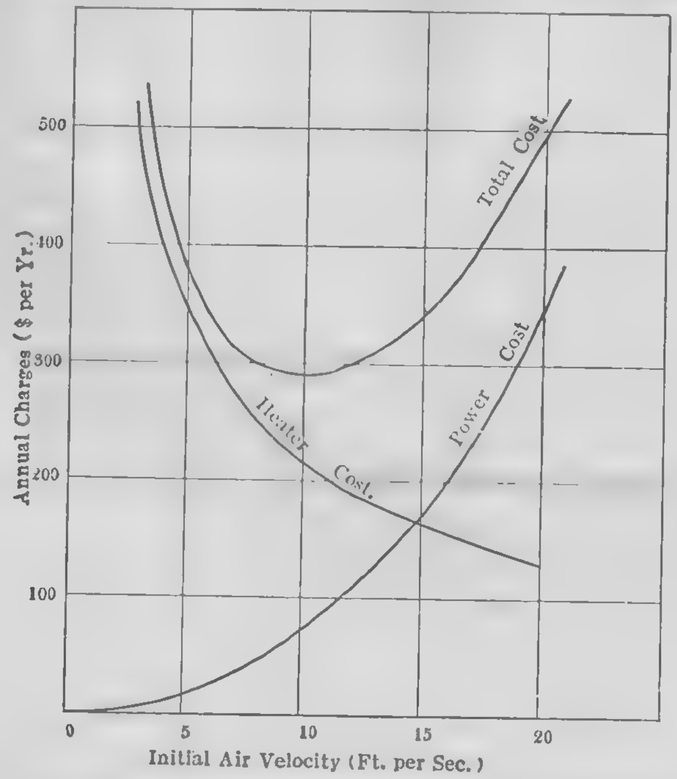


FIG. 40.—Optimum Velocity in an Air Heater (by Economic Balance).

force the air through that heating surface is mounting up every hour of operation.

Note also that the percentage charged off against depreciation and the like is very low. Under conditions where this charge must be higher even lower velocities are desirable but where power is cheaper the reverse would be true. There is often a tendency on the part of the designer to keep down initial investment by an installation that is in reality inefficient because of excessive operating costs.

PART III. RADIATION

A. General Equation for Total Radiation

If energy in the form of radiant heat be allowed to strike a body, either solid or liquid, a certain proportion of the total impinging is reflected from the surface of the body back into the surrounding space, while the remainder passes through the surface into the mass. This entering radiation, in opaque bodies, is absorbed by the body and quantitatively transformed into heat, and in translucent bodies, part is so absorbed and the remainder passes through. For every material that fraction of the total energy impinging on its surface in the form of radiant heat which is absorbed is a constant characteristic for the material. The remainder of the energy is reflected or transmitted. This fraction for any given material varies with the wave length of the radiation, and with the temperature of the surface of the body. When radiant energy is widely dispersed through the spectrum, it is possible to employ for any given body an average value of this coefficient, amply accurate for engineering purposes. So far as determined, this coefficient increases rapidly with the temperature above 1600° C., but does not vary greatly at low temperatures; it will be taken as independent of the temperature for all calculations in this text. Substances for which this fraction has the value unity, namely those absorbing all the radiation striking them and reflecting none, have been given by Kirschoff the name "black bodies," and while it is only under exceptional conditions that such behavior can be quantitatively realized in any solid, the concept of the "black body" is fundamental to an appreciation of the phenomena of interchange of energy in the form of radiation between solids or liquids and their surroundings.

The presence of a gas in the space surrounding a body does not appreciably affect the radiation from the body, and as all gases have very low absorptive powers for radiant energy, it passes through the gas practically undiminished in amount. When absorbed by a surface placed in its path, it will be converted into heat and in this form it can be taken up by the gas by the processes of conduction and convection as already discussed.[1]

We owe to the theoretical and experimental work of Stefan, Boltzmann, Lummer and others, the knowledge of the fact that

[1] However, see p. 165.

the *total* energy radiated per unit surface area for any body which behaves as "black" is entirely independent of the material of the body and is proportional only to the fourth power of the absolute temperature of the body. This is expressed mathematically by the equation,

$$\frac{Q_T}{\theta} = bAT^4. \quad \ldots\ldots\ldots \quad (42)$$

The values of the radiating powers relative to ideal "black" body, p, for various metals are given on p. 184. The available data are meagre and conflicting because in most of the experimental determinations, convection was not eliminated, and the convection corrections were not accurately estimated. The relative radiating powers of most compounds, oxides, salts, organic substances, etc., are not accurately known, and are difficult to measure. The majority may be assumed as approximately 90 per cent "black." Metals, when covered with a continuous rough film of oxide, also may be taken as 90 per cent "black," *i.e.*, their behavior is determined by the composition of their surfaces.

Equation (42), when corrected for relative blackness becomes,

$$\frac{Q_T}{\theta} = bApT^4. \quad \ldots\ldots\ldots \quad (42a)$$

which is the *general* equation from which the *total* radiation *for any case* may be calculated. However, in most cases of industrial importance, one is interested in the *net* radiation, which is obtained by applying Eq. (42*a*) to both the hot and cold bodies, the desired result being obtained by difference. The following special cases deal only with radiation between bodies (solids and liquids) each at a constant temperature.

B. Net Radiation between Bodies (Solids or Liquids) Each at a Constant Temperature

Case I. Two Parallel Planes, Indefinite in Extent.

In this case,

$$\frac{Q_n}{\theta} = A\frac{\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]}{\frac{1}{p_1 c} + \frac{1}{p_2 c} - \frac{1}{c}}, \quad \ldots\ldots \quad (43)[1]$$

[1] In this equation the absolute temperature is divided by 100 before

where Q_n/θ is the *net* loss of heat per unit of time from the hotter body, A is the surface area of either body, p_1 and p_2 are the coefficients of relative blackness of the hotter and colder surfaces at the absolute temperatures T_1 and T_2 respectively, and c is the "black body" radiation coefficient.

In English units c is 0.172 B.t.u./hr./sq. ft./(°F. abs./100)^4 while in c.g.s. units, c is 0.000137 gm. cal./sec./sq. cm./(°C abs./100)^4. The constant b in Eqs. (42) and (42a) is c/100,000,000 in either system of units.

Eq. (43) also applies to two concentric spheres when the diameters are nearly equal, and may be used as an approximation for estimating the transfer of heat by radiation from the hotter to the colder walls in heat recuperators as found in combustion practice, and in concentric pipes.

Case II. A Small Body Completely Surrounded by a Large Body.

It can be mathematically shown that in a space entirely surrounded by a solid at a given temperature, whatever the relative "blackness" and configuration of the inner walls may be, the *combined* radiation and reflection from each unit area of the interior surface is exactly the same as though the body were "black." Moreover, if within this enclosed space there be a relatively small solid body, whether "black" or not, the total radiation striking this body is identical with what it would radiate were it a "black body" at the temperature of its surroundings. In such a case, the energy interchange or *net* radiation, between the enclosed body and its surroundings is given by the equation:

$$\frac{Q_n}{\theta} = A p_e c \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right], \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where p_e is the relative blackness of the enclosed or smaller body and A is the area of the enclosed body.

Illustration 10.—A standard 1-in. steel pipe for sampling gas is placed concentrically within another steel pipe so that cooling water can be circulated in the jacket, the whole projecting 3 ft. into the furnace. If such a combination be inserted into an open-hearth steel furnace whose inner bed and walls are at 1500° C. and where the average gas velocity is 15 ft. per sec. at 1800° C., how much water at 100° F. must be supplied to it, if the water leaves at 180° F.?

raising to the fourth power merely as a matter of convenience to avoid excessively high numbers. (Otherwise the constant would be divided by 100,000,000.)

Solution.—Basis: 1 sq. ft. *outer pipe area.*
The °F. absolute temperature of the furnace wall is

$$(1500)\ (1.8) + 492 = 3190,$$

and the pipe is at an average temperature of 140+460 = 600° F. abs. Since rusty iron is 90 per cent black, the heat transferred to the pipe by radiation (Eq. 44) is 160,000 B.t.u./hr./sq. ft.

Since the gases in the furnace are at 1800° C., and have a velocity of 15 ft. per sec. at this temperature, the heat transferred from the hot gases to the outside of the pipe may be estimated by the equation:

$$Q_n/A\theta = (h_G)\Delta t,$$

where the value for h_G is obtained from Eq. (37). The heat so transferred amounts to only 9050 B.t.u./hr./sq. ft.; small when compared to 160,000.

Since the water has a specific heat of unity and a temperature rise of 80° F., the water supply in gallons per minute to the pipe must be

$$\frac{169{,}000}{(60)\ (80)\ (1)\ (8.33)} = 4.22 \frac{\text{G. P. M.}}{\text{sq. ft. outer pipe surface}}.$$

The pipe sizes must now be chosen so that this much water will be sure to flow at the lowest pressure to which the water may fall. Since the outer pipe is a standard 1-in. steel pipe and projects 3 ft. into the furnace, its outer area is 1.03 sq. ft., which calls for practically 4.4 gallons of water per minute.

An additional illustration is given below under "Radiation Errors in Pyrometry."

Case III. Intermediate Cases.

The total radiation *emitted* by each of the two bodies is independent of the surroundings and may be calculated by Eq. (42a); the radiation *received* by each body is the total radiation emitted by the other body corrected for the average spherical angle subtended. The *net* radiation exchanged between the two bodies may then be obtained by difference. Calculations of this sort are extremely complicated and in practice usually involve rough approximations. For these reasons, no illustrations are given.

Case IV. Two Main Bodies Connected by a Body at Intermediate Temperatures.

Many cases arise in which the body radiating heat and that receiving it are connected by walls at intermediate temperatures, the area of these connecting walls not being negligible in comparison to the area of the hot and cold bodies. An important illus-

tration of this case is found in the coal-fired steam boiler. A large fraction of the heat is generated within the fuel bed and of this a great proportion is transmitted to the boiler by radiation. However, the walls of the boiler setting are large in area in comparison with the surface of the fuel bed and frequently too in comparison with the exposed surface of the boiler. A certain amount of the energy radiated from the fuel bed does go directly to the boiler but a large fraction of it hits the walls of the setting where a part of it is reflected either to other points on the setting, to the boiler or to the fuel bed, while the remainder is absorbed. This absorbed heat raises the walls to incandescence and since the walls are poor conductors most of the energy is re-emitted as radiation. A part of this goes direct to the boiler, another part to other portions of the walls and the remainder to the fuel bed itself. However, in this case the difference in temperature between fuel bed and boiler is so great that the amount of heat returned to the fuel bed is small compared to that emitted, consequently the heat evolved by radiation can be estimated with precision sufficient for engineering work by neglecting these reflection and radiation effects to the wall and calculating the radiation from the surface area of the fuel bed alone. It is immaterial whether the equation for Case I or Case II be employed, as the fuel bed is approximately 90 per cent black and the returned radiation is too small to be anything other than a correction factor.

The Bureau of Mines [1] has carried out a series of experiments in which a Heine boiler was fired with a "dutch oven" located about 40 ft. in front of the boiler and connected with it by a horizontal fire-brick flue 3 by 3 ft. in section. Pyrometers were inserted into this flue at various points and Fig. 41 shows the readings of these pyrometers at various points along the flue (Test 191). There was approximately a 2 per cent air leakage into the flue, but it will be noted that the temperature drop is approximately 21 per cent. As pointed out by the experimenters this drop in temperature along the flue is due to the existence of what may be called a "radiation gradient." Energy is radiated from the oven itself into the first part of the flue raising this to a very high temperature. From here the energy is radiated further down the flue but since the net radiation is in this direction the

[1] U. S. Bureau of Mines, *Bull.* **135**, 1917.

temperatures there must be lower. Again the energy is further radiated down the flue from wall to wall.

It will of course be realized that the readings of these pyrometers do not represent the gas temperature at the point in question (see pp. 166 to 167). However, they would be very close to the temperature of the flue walls but not identical, since the pyrometer tip "sees" both the oven and the boiler more directly than the walls and because the gas velocity in the center of the flue is

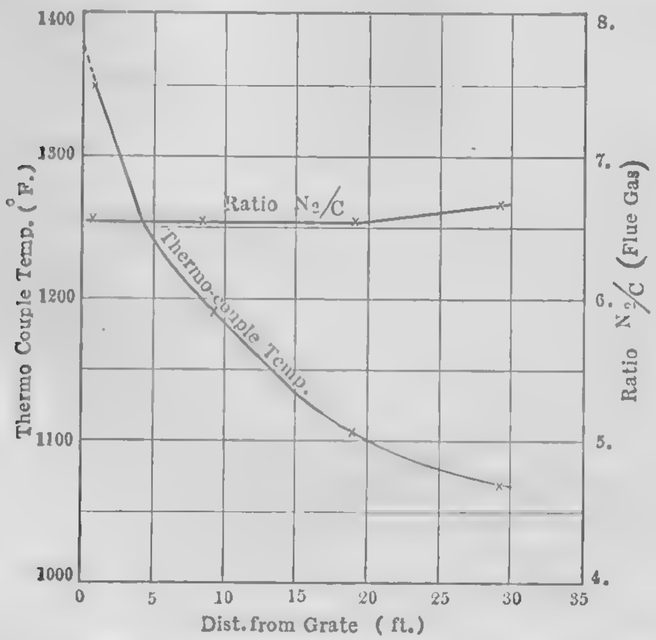


FIG. 41.—Plot Showing Radiation Gradient in Furnace Flue.

greater than that at the walls. The case is obviously a complicated one but the data illustrate very clearly the mechanism of heat transfer by radiation from a hot body along a passage at a somewhat lower temperature to a colder body.

No definite equation can be given to cover such cases; each should be considered separately, or solved by making suitable approximations.

C. Radiation between Solids and Gases

As already stated, the radiation capacity of gases is small compared to that of solids. Furthermore, gaseous radiation

is in the form of bands of limited width, the wave length of the bands being characteristic of the gas in question. Consequently, radiation interchange between gases and solids is negligible as compared with the radiation between two solids at different temperatures, if the gases are at approximately the same temperature as the solids. If, however exceedingly hot gases are in sight of relatively cold solids, the heat transferred from the gases to the solids by radiation may be large compared to that by conduction and convection. When h_c is high, gaseous radiation is usually small in comparison with that transferred by convection.[1]

D. Radiation Errors in Pyrometry

An ordinary mercury thermometer or a thermocouple is often used to measure the temperature of a gas when the temperature of the surroundings is different from that of the gas. Under such conditions the thermometer will indicate an apparent gas temperature somewhere between that of the gas and the surroundings: if the gas be the hotter, the thermometer reading will be too low, and if the wall be the hotter, the reading will be too high. The factors which tend to develop a large error are: large difference between the true temperature of gas and surroundings, high temperature of either the thermometer or the surroundings, and low gas velocity.

The mechanism by which the error is developed may be illustrated by considering a thermocouple inserted in the gas stream passing through a duct, the walls of which are hotter than the gas, under conditions such that the true temperatures of the walls and gas remain constant. The walls radiate heat to the couple, which tends to raise its temperature, but the couple loses heat to the gas stream by conduction through the gas film on the couple and thence by convection to the main body of the gas. These two opposing factors soon counterbalance, thereby establishing a constant reading on the couple. Under this condition of dynamic equilibrium the rate of heat flow by radiation must be exactly equal to that by conduction and convection, as otherwise the temperature of the couple would change. The method of calculation is simple; the observations required are the temperatures of the wall and thermocouple and the gas velocity, the

[1] See however, Nusselt, *Zeit. Ver. deut. Ing.*, **67** (1923), 692; see also *Mech. Eng.*, **48**, No. 10 (October, 1926), 1047.

latter being required in the calculation of the coefficient (h_G) between gas and couple. The auxiliary data necessary are relative blackness (p) of couple and an equation from which h_G may be calculated. Unfortunately, data concerning the values of p for glass thermometers are meager, and hence exact calculations are impossible. None the less, estimation of the error is often worth while, as it may be as high as several hundred degrees in some cases. For the ordinary glass and mercury thermometers, a value of p of 0.60 is suggested, while for thermocouples, covered with a film of oxide, the value of 0.90 is recommended. For estimation of h_G, the use of Eq. (37) is suggested for air or flue gas.

Illustration 11.—The temperature of the air at a certain point in a blast furnace stove is measured as follows:

A thermocouple is inserted into the flue space, and reads 650° C.; the neighboring bricks are found by an optical pyrometer to be 700° C. The air enters the base of the above at 70° F., with a velocity of 4 ft. per sec. The outside diameter of the thermocouple well is ½ in.

What is the true air temperature at the point in question?

As soon as constant conditions have been established the net radiation gained by the couple from the hotter walls just equals the heat lost by convection by the couple to the cooler air. Calling the true air temperature t° C., the couple 90 per cent black body (due to its oxide coating), one obtains by equating (44) and (26);

$$Q_n/A\theta = (0.9)0.172[(17.5)^4 - (16.6)^4] - h_G(1.8)\ (650 - t).$$

h_G is obtained by Eq. (37). For this equation,

$$v = (4)\frac{(492)\ (29)}{(530)\ (359)} = 0.3 \text{ lbs. per sec. per sq. ft.}$$

so that $h_G = 6.4$. Whence the true gas temperature at this point (t) = 410° C., which is quite different from the apparent temperature of 650° C.

E. Simplified Radiation Equation: First Power of Temperature Difference

When a hot body, small in size compared to its surroundings, is exposed to a cooler gas, it loses heat not only by conduction through and convection from the gas film on its surface, but also by radiation to the surroundings in accordance with Eq. (44). The total heat loss can, therefore, be obtained by adding Eqs. (26) and (44).

$$\frac{Q_n}{A\theta} = h_G(\Delta t) + p_1 0.172\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]. \quad . \quad . \quad . \quad (45)$$

However, this is a case of *parallel flow*, and it would be most convenient to calculate the heat loss by the equation

$$Q_n/A\theta=(h_c+h_r)\Delta t, \quad \ldots\ldots\ldots (46)$$

where Δt is the °F. temperature difference between the *surface* of the hot body and the walls of the enclosed space, and h_r is the

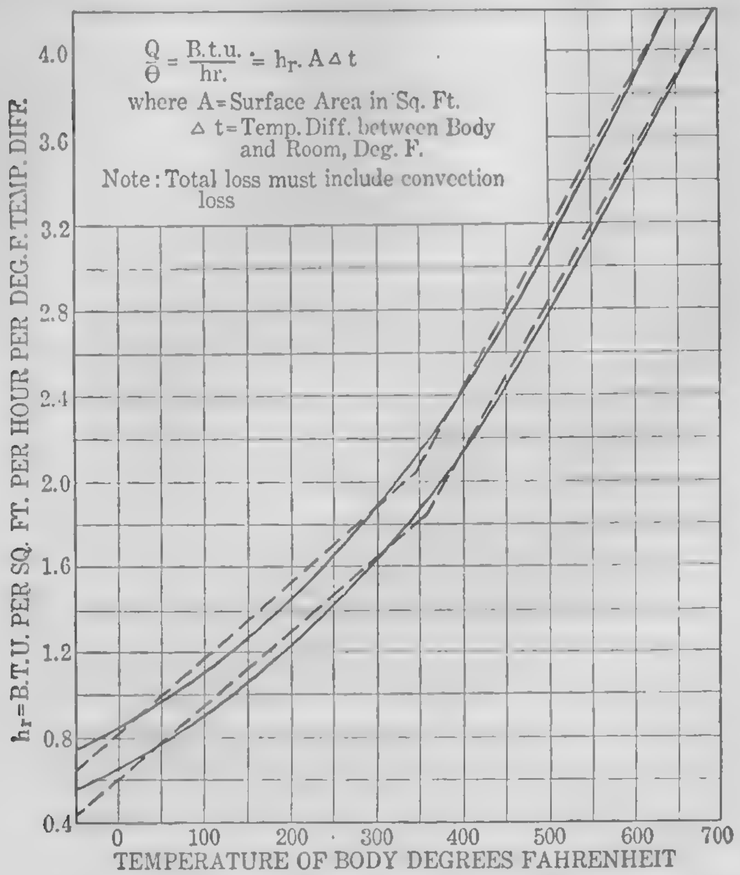


FIG. 42.—Radiation Coefficient (h_r) from a Relatively Small Black Body to a Room.

radiation coefficient for Eq. (46). This may be calculated by assuming that over a definite temperature range the actual fourth power equation may, as an approximation, be represented as proportional to the temperature difference. This simplification is merely a method of convenience.

$Q_u/A\theta$ (by radiation only) $=p_1c[(T/100_1)^4-(T_2/100)^4]=h_r(\Delta t)$,

which when solved for h_r gives

$$h_r=\frac{p_1c}{(t_1-t_2)}\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right] \quad \ldots\ldots\ldots (47)$$

Figure 42 shows how h_r for a black body, small in size compared to the walls, increases with the temperature of the black body, when the walls of the enclosed space are 70° or 0° F. For a body having a relative coefficient of blackness, p, h_r for such a body is p times that shown in the plot.

F. Coefficient of Surface Loss by Radiation and Convection (h_c+h_r)

Figure 43 shows values of this joint coefficient for bare pipes exposed to a room at 70° F. This coefficient increases with, but

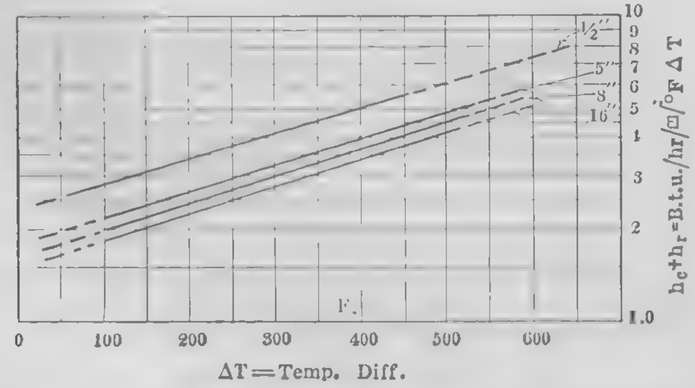


FIG. 43.—Coefficient of Heat Transfer by Radiation Plus Convection (h_c+h_r) from Bare Pipes to a Room at 70° F.

Data for 5″ pipe from McMillan, *Trans. A. S. M. E.*, **37**, (1915). Data from ½″, 8″, and 16″ pipe from Paulding, "Steam in Covered and Bare Pipes," Van Nostrand, New York.

not in direct proportion to, the difference in temperature between the *surface* of the pipe and that of the room. By the use of semi-logarithmic paper, the data fall on straight lines, as shown in Fig. 43, making extrapolation reasonably safe. Although these data were determined for bare pipes, which are probably 90 per cent "black" because of oxide coating, they may be used as an approximation for lagged pipes, where p is again about 0.90.

Illustration 12.—Estimate the heat loss per 24 hrs. from 100 linear feet of standard 1-in. steel steam pipe at 370° F. to a room at 70° F.

Solution.—As shown by Fig. 43, h_c+h_r equals 4.0. By Eq. (46)

$$Q=\frac{(24)\ (4.0)\ (1.315)\ (3.14)\ (100)\ (370-70)}{12}=990{,}000 \text{ B.t.u.}$$

Since the effect of diameter on the joint coefficient is not marked, additional lines may be drawn for other diameters which will be sufficiently precise for approximate work.

Illustration 13.—Calculate the temperature drop from steam to outer pipe surface in the preceding example.

Solution.—Basis: 1 sq. ft. outer pipe surface.

$$\text{By Eq. (46), } \frac{Q}{A\theta} = (4.0)\ (370-70) = 1200 \text{ B.t.u. per hr. per sq. ft.}$$

This same heat flows through the condensing steam film inside and then through the tube wall.

$$\frac{Q}{A\theta} = \frac{\text{Temperature steam} - \text{Temperature outer wall}}{\dfrac{1}{(h_1)\ (A_1)} + \dfrac{L_2}{(k_2)\ (A_2)}}.$$

Now, h_1 for the steam film is 2000, A_1 is $1.05/1.315(1) = 0.799$ sq. ft., the wall thickness is 0.133 in., $k = 25.0$, and the average area (A_2) is

$$0.5(1.315+1.05)/1.315 = 0.902 \text{ sq. ft.}$$

whence the temperature drop from steam to outer pipe is 1.3° F.

In the preceding problem the steam was therefore at 371° F. and only 1° of the 301° F. total drop was due to the combined resistances of condensing steam film and metal wall. In other cases, such as in a surface condenser for steam, the other series resistances are less in comparison to that of the steam film and a much greater temperature drop is found through the steam film than in the preceding example.

G. Principles Utilized in Radiation Pyrometry

At very high temperatures the radiation from all bodies is approximately black, while the radiation from a body in an entirely closed space, the whole system being at the temperature to be measured, is quantitatively black. An opening in the surrounding space, provided it be small, does not appreciably affect the radiation. This makes it possible to realize so completely black body radiation in the measurement of high temperatures that the energy emitted can be used as a quantitative measure of the temperature. The total radiation can be determined with a bolometer, or, what is more convenient, the amount of energy

emitted of some definite wave length chosen from the visible spectrum may be measured by photometric means as in the Wanner pyrometer.

It is also possible to match the color of the light emitted with that of a lamp filament, determining its temperature from the current consumption. This color rapidly whitens at higher temperatures due to great preponderance of the blue. Many other methods are available which have not hitherto been reduced to practical application, *e.g.*, the determination of the wave length of greatest energy, this wave length decreasing rapidly with rise in temperature.

PART IV. LOGARITHMIC MEAN TEMPERATURE DIFFERENCE

Case I. Where the temperature difference between the two bodies to and from which heat is flowing varies with the time.

When heat is flowing from one body to another through a resistance, the amount of heat transferred is proportional to the temperature difference, *i.e.*, $Q/\theta = \Delta t/R$. When the temperature difference between the two bodies to and from which heat is flowing varies with the time, the true mean temperature difference for the duration of time in question is given by the expression:

$$(\Delta t)_{av} = \frac{\Delta t_1 - \Delta t_2}{2.3\ log_{10}\left(\dfrac{\Delta t_1}{\Delta t_2}\right)}, \quad \ldots\ldots\ (52)$$

where Δt_1 is the temperature difference at the start, and Δt_2 is the temperature difference at the end of the time. In the derivation of this equation, which is given on pages 185 to 187 the following assumptions are made:

1. At any particular instant every part of the two bodies from and to which heat is flowing is at a uniform temperature. Such conditions are found only in metals and fluids. In metals, the conductivity is so high compared to that of the boundary that the temperature of all parts of the metal at any time is practically the same. In a fluid, although the conductivity is very low, the uniform temperature at any point is quickly brought about by convection currents.

2. The specific heat of each body is constant throughout the temperature range under consideration.

3. The resistance to the flow of heat is constant throughout the operation.

4. The heat capacity of the boundary is negligible in comparison to the heat capacities of the bodies to and from which heat is flowing.

While all of these assumptions are not rigidly true in the cases met in practice, especially the third, yet this log mean equation is a good approximation for mean temperature difference for all cases of intermittent heating and cooling. For example, in quenching steel billets in oil, the temperature difference between steel and oil is high at the start and considerably less at the end. Or, where cold liquor in an intermittent [1] preheater is being warmed by steam in closed coils similar initial and final conditions exist.

Case II. Where the temperature difference varies at different points in the apparatus.

This log mean equation also gives the true average temperature difference for the case where the temperature difference is constant with respect to time, but varies with space. (See Figs. 44 and 45.) That is, the temperature difference is at all times constant at any particular point in the system, but varies with respect to the location of the section chosen. In other words, if the temperature difference between two bodies flowing continuously through a system be called Δt_1 at one end of the system and Δt_2 at the other end, then the true mean temperature difference at all times for the entire system is as before:

$$(\Delta t_{av}) = \frac{\Delta t_1 - \Delta t_2}{2.3 \log_{10}\left(\frac{\Delta t_1}{\Delta t_2}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

The limitations for this case are similar to those for Case I:

1. At any particular cross-section of the apparatus, taken perpendicular to the direction in which the bodies are flowing, the temperature difference must remain constant, although it varies with the point chosen.

[1] A preheater to which no liquor is added or removed is called an "intermittent" one in contra-distinction to the "continuous" type, where the liquor is fed in and removed continuously.

2. The specific heat of each body must be constant throughout the temperature change which it undergoes.

3. The resistance to heat flow at each point in the apparatus must be the same as at every other point. (In this case heat capacity is not a factor, the heat content at each point in the boundary remaining constant.)

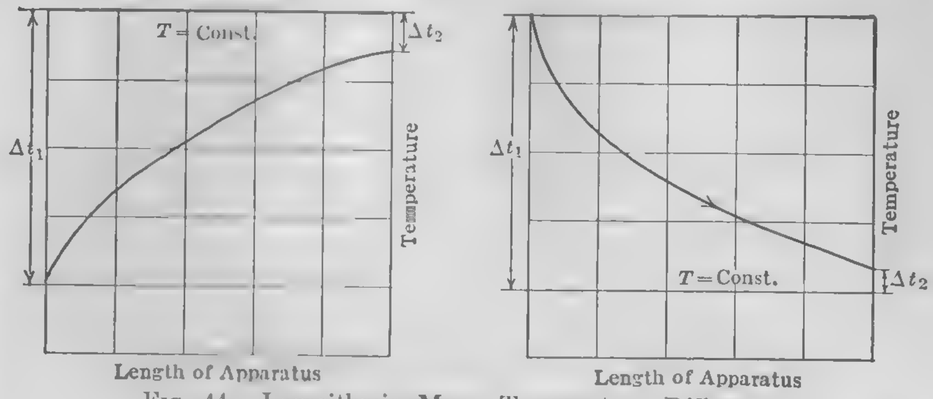


FIG. 44.—Logarithmic Mean Temperature Difference.
A. Preheater or Condenser. *B*. Cooling of One Fluid by Evaporation of Other Fluid.

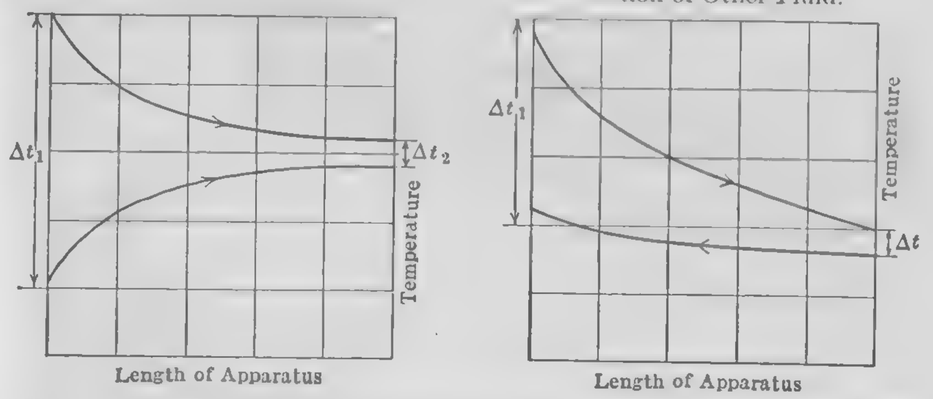


FIG. 45.—Logarithmic Mean Temperature Difference. *A*. Parallel-flow Heat Interchanger; *B*. Counter-flow Heat Interchanger.

The derivation for the equation in this case is similar to the derivation for the case where the temperature difference changes with the time.

As in the preceding case, all assumptions are not rigidly accurate, but this logarithmic expression for the mean temperature difference between two bodies in a continuous apparatus is a good approximation and has a wide application in problems of heat transfer.

For example, consider an apparatus where hot oil is being cooled from 150 to 25° C. by means of water which flows countercurrently by entering at 20 and leaving at 70° C. The temperature differences are 80 and 5° C. at the ends of the apparatus, so that, by Eq. (52),

$$(\Delta t)_{av} = \frac{80 - 5}{2.3 \log_{10} \frac{80}{5}} = 27.1° \text{ C.}$$

The ordinary arithmetic mean gives 42.5° C., which is 57 per cent higher than the more nearly correct value of 27.1° C.

Δt is the temperature difference at some *point* in a continuous apparatus, or at some *time* in a discontinuous apparatus; the true mean difference will not be obtained if the difference of the logarithmic mean temperatures is taken. For example, in the preceding illustration, the respective logarithmic mean temperatures of the oil and water are 69.9° and 39.9° C., and the difference is 30° C.

The log mean temperature difference with the above limitations is ordinarily used for the following types of commercial equipment: coolers or heaters for gases and liquids, furnace regenerators and recuperators, kilns heated by hot gas, boiler feed-water heaters, heat interchangers, economizers, condensers, driers, humidifiers, the cooling and heating of intermittent furnaces, etc.

It will be noted that the logarithmic mean temperature difference is always less than the arithmetic mean:

$$\Delta t_{av} = \frac{\Delta t_1 + \Delta t_2}{2} \quad \ldots\ldots\ldots \quad (52a)$$

By substitution in Eq. (52) it is found that when the ratio of the temperature differences is less than two, the arithmetic mean value is only 4 per cent higher than the logarithmic value. As this accuracy is sufficient for most engineering problems in heat flow, the arithmetic mean may be used when the ratio of the temperature differences is not greater than 2, even though the logarithmic mean theoretically applies.

PART V. SUMMARY OF EQUATIONS, TABLES OF DATA, NOMENCLATURE, AND CONVERSION FACTORS

The following summary is given for use in the solution of problems. The equations given herein include the more important of those already given. A table of symbols with the corresponding values in the English and c.g.s. systems is also given, and this is followed by a summary of the more important data, and suitable conversion factors.

Summary of More Important Equations

Heat transfer from one fluid through a solid retaining wall or tube, to another fluid.

$$\frac{Q}{\theta} = \frac{\Delta t}{\frac{1}{h_1 A_1} + \frac{L_2}{k_2 A_2} + \frac{1}{h_2 A_3}} = \frac{\Delta t}{R} \quad \ldots\ldots \quad (27)$$

The following illustrations of applications of this equation have been given:

From	Through	To	Page
Moving liquid	Metal	Moving liquid	143
Condensing steam	Metal	Boiling liquid	145
Moving gas	Metal	Moving water	149
Condensing steam	Metal	Moving air	153
Condensing vapor	Metal	Moving water	157

Heat transfer from one fluid through several insulating walls to another fluid.

$$\frac{Q}{\theta} = \frac{\Delta t}{\frac{1}{h_1 A_1} + \frac{L_2}{k_2 A_2} + \frac{L_3}{k_3 A_3} + \frac{L_4}{k_4 A_4} + \frac{1}{h_5 A_5}} = \frac{\Delta t}{R} \quad \ldots \quad (27a)$$

Equations for area of heating surface:

For flat walls, $A = A_1 = A_2$.

For walls of circular section, where the outer diameter is not more than twice the inner,

$$A = \frac{(A_1 + A_2)}{2} \quad \ldots\ldots\ldots \quad (10a)$$

For walls of circular section, where the outer diameter is more than twice the inner,

$$A=\frac{A_2-A_1}{2.3\,log_{10}\left(\frac{A_2}{A_1}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

For rectangular bodies, where the walls are more than twice as thick as the shortest inside dimension, the equations developed by Langmuir should be used, see pages 129 to 131.

Equations for temperature difference:

Where Δt varies, but Δt_1 is not greater than twice Δt_2,

$$\Delta t=\frac{\Delta t_1+\Delta t_2}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52a)$$

Where Δt varies, and Δt_1 is greater than twice Δt_2,

$$\Delta t=\frac{\Delta t_1-\Delta t_2}{2.3\,log_{10}\left(\frac{\Delta t_1}{\Delta t_2}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

A list of cases where this equation may apply is found on p. 174.

Heat flow by radiation only, where the body is large compared to the surroundings,

$$\frac{Q_n}{\theta}=\frac{cA\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]}{\frac{1}{p_1}+\frac{1}{p_2}-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Heat flow by radiation only, where the body is small compared to the surroundings,

$$\frac{Q_n}{\theta}=p_e cA[(T_1/100)^4-(T_2/100)^4]. \quad . \quad . \quad . \quad . \quad (44)$$

For application, see examples on p. 163.

When the temperature of the radiating surface is below 700° F., the radiation loss is figured more conveniently by the simplified methods given on pp. 167 to 170.

Total heat flow (including radiation) for any case.

According to conditions, this is given by one of the following combinations: (27) plus Q/θ calculated from either (43) or (44). For application, see pp. 163 to 170.

Summary of More Important Data

All the data given in this table are in English units as defined in the Nomenclature Table, page 178.

Conduction through a solid of known thickness. (See Table I, pages 181 and 183.)

Solids to Gases

From solid surface to "still air," natural convection:

From vertical walls to a room at 70° F.,

$$h_a=0.7+\frac{(\Delta t)}{(375)}, \text{ for values of } \Delta t \text{ from 10 to 500° F} \quad . \quad . \quad . \quad (34)$$

For convection upwards from horizontal walls, increase (34) by 10 per cent.

For convection downwards from horizontal walls, decrease (34) by 50 per cent.

For gases flowing in turbulent motion inside pipes or in annular spaces:

$$h_a=\frac{0.22C_pT_f^{3/4}v^{0.8}}{D^{0.2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)^1$$

For air flowing in turbulent motion at right angles to single pipes:

$$h_a=\frac{0.8T_f^{1/3}v^n}{D^{0.53}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)^2$$

where $n=0.60+0.08\ \log_{10}D$. Data for staggered pipes are given on page 152.

Solids to Liquids—Liquids not Boiling

For natural circulation (important variables: temperature difference, viscosity, thermal conductivity of liquid, shape of vessel, and condition of heating surface).

[1] Equation 35 is based on data for air, carbon dioxide, and illuminating gas for the following conditions: v from 0.2 to 30 lb. per second per square foot of free area, D from 0.3 to 4 in., T_f from 630 to 1650° R. See pp. 148 and 140–142.

[2] Equation 37 is based on data for air for the following conditions: v from 0.01 to 11, D from 0.001 to 2, and T_f from 595 to 1410.

Nomenclature

Symbol	Meaning	Units	
		English Units	C. G. S. Units
A	Area[1]	Sq. Ft.	Sq. cm.
b	"A constant"		
c	Radiation coefficient	0.172	0.000137
C_p	Sp. ht. at constant pressure[2]	A ratio	A ratio
D	Actual inside diameter of pipe	Inches	
d	Outside diameter of insulation	Feet	
f	"A constant"		
H	Overall series coefficient	B.t.u./hr./sq. ft./°F.	Gm. cal./sec./sq. cm./°C.
h	Film coefficient	B.t.u./hr./sq. ft. per °F.	Gm. cal./sec./sq. cm./°C.
h_r	Surface coefficient for first power radiation, Eq. (46)	B.t.u./hr./ sq. ft. per °F.	Gm. cal./sec./sq. cm./°C.
k or K	Coefficient of heat conductivity	B.t.u./hr., sq. ft./°F. ft.	Gm.cal., sec., sq.cm./°C./cm.
L	Distance[3]	Feet	Centimeters
N	Total length	Feet	Centimeters
p	Relative "blackness" compared to the ideal "black body"	0 to 1	0 to 1
Q	Quantity of heat	B.t.u.	Gm. cal.
Q_n	Net quantity of heat	B.t.u.	Gm. cal.
J	Fluidity of fluid (reciprocal of viscosity) relative to water at 68° F. (20° C.)	No units	No units
M	Average molecular weight	A ratio	A ratio

Nomenclature, continued

Symbol	Meaning	Units	
		English Units	C. G. S. Units
T	Absolute temperature[4]	°F. abs.	°C. abs.
R	Total series resistance	Σr	Σr
r	Individual resistance	L/kA or $1/hA$	L/kA or $1/hA$
s	Sp. gr. (relative to water as unity)	A ratio	A ratio
t	Temperature	°F.	°C.
θ	Time	Hours	Seconds
Δt	Temperature difference	°F.	°C.
u	Average linear velocity	Ft./sec.	
$v = u\rho$	Average mass velocity	Lbs./sec./sq. ft. free area	
w	Mass velocity at line of pipe centers	Lbs./sec. per sq. ft	
ρ	Fluid density	Lbs./cu. ft.	
dQ	Differential quantity of heat		
dt	Differential temperature		
dL	Differential distance		
$d\theta$	Differential time		

[1] Taken always *at right angles* to the direction in which the heat is flowing.
[2] This may be expressed as B.t.u./lb./°F. or gm. cal./gm./°C.
[3] Always taken *parallel* to the direction in which heat is flowing.
[4] °F. abs. = °F. + 460; °C. abs. = °C. + 273.

For water $h = 50$ to 300; see also Eq. (30), p. 139.

For more viscous liquids $h = 10$ to 50.

For forced circulation of liquids above critical velocity; see pages 139 to 144 for data and discussion.

Solid to Liquid—Liquid Boiling

Few direct measurements have been made for such films; from the available data ($H = 180$ to 900) on the overall coefficient from condensing steam through a metal wall to a boiling liquid, it is estimated that the individual coefficient of the liquid film between the solid and the boiling liquid varies from 200 to 4000 depending on

(*a*) the temperature difference between metal and liquid,

(*b*) the arrangement of heating surface,

(*c*) the condition of the heating surface, *i.e.*, whether covered with crystals, scale, etc.,

(*d*) viscosity and density of the boiling liquid, and

(*e*) whether or not the liquid is stirred, or circulated by means of a pump.

For data on enameled apparatus, heated by steam or by hot oil, see p. 146.

Condensing Vapor to Solid

Data for steam only are available. The coefficient for a condensing steam film varies from 3000 to 10 as the percentage of non-condensable gas in the steam increases from zero to 100 per cent. For steam containing little air, as in good engineering practice, $h_v = 2000$. For *other* vapors, as an approximation, $h_v = 2200\ KJ$.

Thermal Conductivities of Liquids[1]

In 1893 H. F. Weber[2] derived a relation for correlating the specific thermal conductivities k of liquids with specific heat c, specific gravity s, and molecular weight M, giving $k = 0.86\ cs\sqrt[3]{s/M}$. Thus the value of k for water predicted from this equation is $k = 0.86\ (1)\ (1)\ \sqrt[3]{1/18} = 0.33$, which checks well with the value of 0.35 given by Bridgman for 86° F. (see Table 1, p. 182). As the temperature was increased from 86 to 167° F., Bridgman found that for 11 different liquids k decreased slightly but k for water increased 7 per cent.

[1] McAdams and Frost, *J. Ind. Eng. Chem.*, 11 (1922), 16.

[2] *Wied. Ann.*, **48** (1893), 173.

TABLE I

Coefficient of Heat Conductivity of Solids *

k = (B.t.u.)(ft. thickness)/(hr.)(sq. ft.)(deg. F.)

(a) Metals

Material	Experimental Temperature Range °F.	k	Reference Number
Aluminum	32–212	85	1
Brass, yellow	32–212	55	1
Copper, pure	at 68	238	1
Iron:			
Pure	at 76	37	1
Wrought	32–527	40	1
Cast, 3.5 per cent C	at 86	36	1
Lead	at 59	20	1
Nickel	68–392	32	1
Platinum	64–212	41	1
Silver	at 64	243	1
Steel	at 82	25 §	
Tin	at 32	35	1
Zinc	at 64	64	1

(b) Non-Metals

Asbestos	100–1000	0.12	2
Brick:			
Carborundum	at 1800	5.6	2
Building	at 1800	0.8	2
Kieselguhr	at 1800	0.4	2
Sil-O-Cel	at 1800	0.03	2
Brick and mortar wall	.....	0.4†	
Portland cement, neat	at 95	0.5	2
Cork	122–392	0.03	2
Electrode carbon	212–1700	32‡	2
Glass, flint	50–59	0.3	2
Infusorial earth (12.5 lbs. per cu. ft.)	at 122	0.05	2

* The presence of impurities, especially in the metals, may cause variation in the coefficient of conductivity of almost 100 per cent.

† Average of results from several sources.

‡ The coefficient of conductivity of this material is given as only 10 per cent of this value by other experimenters.

§ This is the lowest value usually quoted.

[1] "Landolt-Börnstein Tabellen," 1905 Ed.

[2] Carl Hering, *Met. and Chem. Eng.*, **9**, 652 (1911).

TABLE I—*Continued*

Material	Experimental Temperature Range °F.	k	Reference Number
Leather	72–97	0.1	1
Mineral wool	70–350	0.03	2
Magnesia	68–310	0.04	2
Rubber	at 220	0.1	1
Sand	68–310	0.2	2
Wood, pine:			
Parallel to fibres	.....	0.07	1
Perpendicular to fibres	.....	0.02	1

(c) Gases

	k		Reference Number
	At 32° F.	At 212° F.	
Air	0.0137	0.0174	3
Carbon monoxide	0.0131	.....	3
Carbon dioxide	0.00804	0.0120	3
Oxygen	0 0138	0.0180	3
Nitrogen	0.0138	0.0174	3
Hydrogen	0.092	0.123	1
Methane	0.0174	.....	3
Steam	0.0095	0.0129	4

[1] "Landolt-Börnstein Tabellen," 1905 Ed.
[2] CARL HERING, *Met. and Chem. Eng.*, **9**, 652 (1911).
[3] Smithsonian Tables, p. 217, 1920 Ed., Smithsonian Inst., Washington, D. C.
[4] MARKS' Mechanical Engineers' Handbook, p. 306, 1916 Ed., McGraw-Hill Book Company, Inc., New York.

(d)[5] Liquids

	k		Reference Number
	At 86° F.	At 167° F.	
Normal pentane	0.078	0.074	5
Kerosene	0.086	0.081	5
Petroleum ether	0.075	0.073	5
Methanol	0.122	0.119	5
Ethanol	0.104	0.100	5
Isopropanol	0.089	0.088	5
Normal butanol	0.097	0.094	5
Iso-amyl alcohol	0.086	0.084	5
Ethyl-ether	0.079	0.075	5
Acetone	0.103	0.097	5
Carbon bisulfide	0.092	0.087	5
Water	0.347	0.372	5

[5] BRIDGMAN, *Proc. Am. Acad. Arts. Sci.*, **59**, No. 7 (December, 1923), 111.

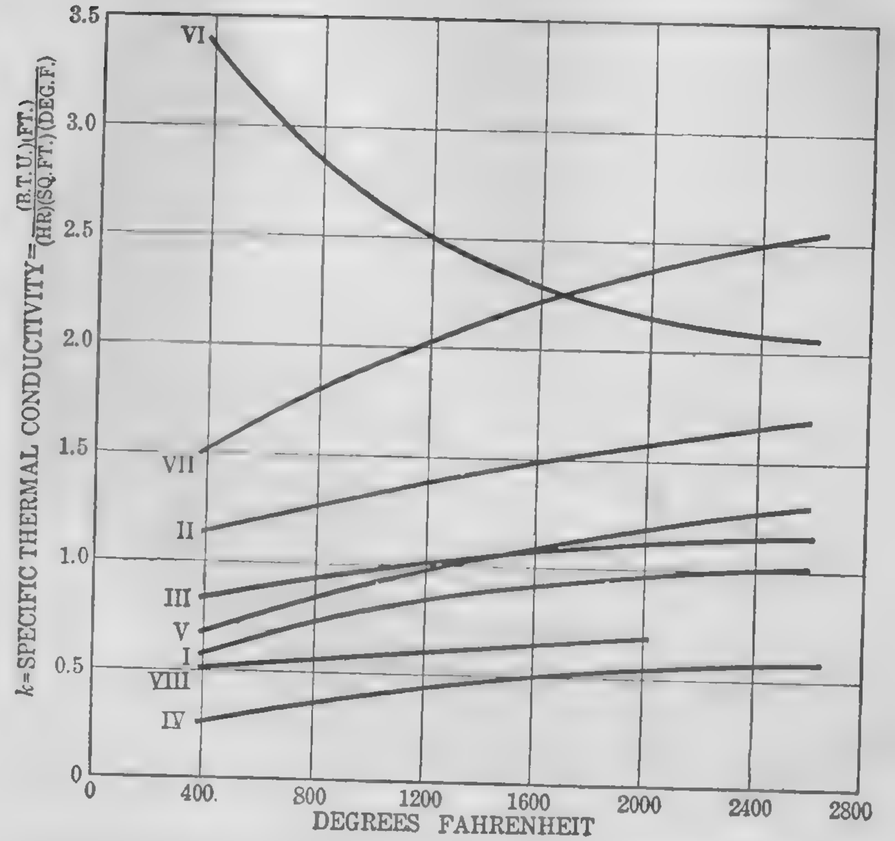


FIG. 45A.—Thermal Conductivity of Bricks *vs.* Temperature (*Norton*).[1]

Curve	Material	Per Cent Porosity
I	Missouri fire brick	18.4
I	Pennsylvania fire brick	26.7
II	Kaolin brick	10.8
III	Kaolin brick	23.2
IV	Kaolin brick	49.1
V	Silica brick	30.4
VI	Magnesite brick	31.6
VII	Fused alumina brick	21.3
VIII	Concrete wall (1:2:4 mixture)	

[1] F. H. NORTON, *Jour. Am. Cer. Soc.*, **10**, No. 1 (January, 1922), 30. This article also gives data for other refractories. *Courtesy Am. Cer. Soc.*

TABLE III

RELATIVE RADIATING POWER OF SOLIDS BELOW 1600° C.
Ideal Black Body..... 1.0

(a) Metals

	Average Value (=p).	Reference Number.
Iron, cast and bright	0.22	1
Iron, oxidized	0.62	1
Iron, or steel, polished	0.20	2
Iron, or steel, highly oxidized	0.90*	
Copper, polished	0.10*	
Copper, calorized	0.26	1
Copper, oxidized	0.72	1
Aluminum paint	0.50	1
Gold enamel	0.37	1
Monel Metal	0.43	1
Silver	0.03	1
Gold, polished	0.05*	
Brass, bright	0.07*	
Brass, dull	0.23	2
Zinc, bright	0.10*	
Zinc, dull	0.22	
Tin, polished	0.10*	
Nickel	0.35*	
Mercury	0.23*	
Platinum	0.24*	

[1] LANGMUIR, *Trans. Am. Electrochem. Soc.*, **23** (1913).
[2] WAMSLER, *Mittellungen über Forschungsarbeiten*, Heft **98** (1911).
* Average of values given by various authorities.

(b) Non-metals

The relative radiating powers of most inorganic compounds (oxides, salts, etc.) and organic compounds are not accurately known. The majority may be assumed as 90 per cent black, *i.e.*, $p=0.90$.

NOTE.—A suitable factor of safety must be introduced to offset the uncertainty in these values.

CONVERSION FACTORS FOR COEFFICIENTS

It will be noted that all data for coefficients given in this chapter have been expressed in "English" units, defined as

B.t.u./hr./sq. ft./°F./ft. thickness for the coefficients of thermal conductivity (k) through solid,[1] and B.t.u./hr./sq. ft./°F. for surface or the "surface film" coefficient (h)[2].

If the coefficient of conductivity (k) is expressed in c.g.s. units, defined as gm. cal./sec./sq. cm./°C./cm. thickness, this c.g.s. value must be multiplied by 242 to convert it to the above English system.

Likewise, a "surface" or "surface film" coefficient expressed in c.g.s. units, defined as gm. cal./sec./sq. cm./°C. must be multiplied by 7370 to convert it to the above English system.

The radiation coefficients in both these systems have been given on p. 162.

Derivation of Equation for Logarithmic Mean Temperature Difference

Assume a system where heat is flowing from one body at a temperature T into another body at a temperature t, and where there is no heat interchange with the surroundings. For the sake of definiteness, consider a hot piece of steel immersed in oil, the walls of the oil container being so well insulated that the loss of heat to the surroundings is negligible. Let the steel have a weight W and a constant specific heat C. At the start when the time θ is zero, the temperature of the steel is T_1, and when the time has any value θ its temperature is T. The heat lost by the steel up to the time θ is therefore, $WC(T_1-T)$. If the oil has a specific heat of c, a weight w and is warmed from t_1 to t in the time θ, the heat gained by the oil is $wc(t-t_1)$. Since there is no heat lost to the surroundings, the heat lost by the steel equals the heat gained by the oil:

$$Q=WC(T_1-T)=wc(t-t_1), \quad \ldots\ldots\ldots (a)$$

or

$$T=T_1+\frac{wc(t_1-t)}{WC} \quad \ldots\ldots\ldots (b)$$

By Newton's law, the heat transferred is proportional to the area, temperature difference and the time.

$$dQ=HA(T-t)d\theta=wcdt, \quad \ldots\ldots\ldots (c)[3]$$

where H equals the overall coefficient of heat transfer from steel

[1] Also through stationary fluids where the thickness is taken into account.
[2] H, the overall value, is also expressed in these units.
[3] The derivation neglects the temperature drop through the steel and the main body of the oil.

to oil, and A is the area of the surface of the steel. Substituting in (c) the values of T found in (b), and rearranging

$$\left(\frac{wc}{WC}+1\right)\frac{HAd\theta}{wc}=-\frac{d\left[-\left(\frac{wc}{WC}+1\right)t\right.}{T_1+\frac{wct_1}{WC}-\left(\frac{wc}{WC}+1\right)t} \quad . \quad . \quad . \quad (d)$$

Integrating (d) between the limits O and θ corresponding to t_1 and t_2.

$$\left(\frac{wc}{WC}+1\right)\frac{HA\theta}{wc}=-ln_e\left[T_1+\frac{wct_1}{WC}-\left(\frac{wc}{WC}+1\right)t_2\right]$$

$$+ln_e\left[T_1+\frac{wc}{WC}t_1-\left(\frac{wc}{WC}+1\right)t_1.\right] \quad . \quad (c)$$

Rearranging (c)

$$\frac{HA\theta}{wc}=\frac{1}{\left(\frac{wc}{WC}+1\right)}ln_e\left\{\frac{[T_1-t_1]}{\left[T_1-t_2+\frac{wc}{WC}(t_1-t_2)\right]}\right\} \quad . \quad . \quad (f)$$

Calling $(\Delta t)_{av}$ the true mean temperature which will give the correct heat flow,

$$Q=(H)\ (A)\ (\theta)\ (\Delta t)_{av}=wc(t_2-t_1), \quad . \quad . \quad . \quad . \quad (g),$$

or

$$(t_2-t_1)/(\Delta t)_{av}=HA\theta/wc. \quad . \quad . \quad . \quad . \quad . \quad . \quad (h)$$

Equating the total heat lost by the steel to that gained by the oil up to the time θ,

$$WC(T_1-T_2)=wc(t_2-t_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

or

$$wc/WC=(T_1-T_2)/(t_2-t_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (j)$$

Substituting (h) and (j) in (f)

$$\frac{t_2-t_1}{(\Delta t)_{av}}=\frac{1}{\left(\frac{T_1-T_2}{t_2-t_1}+1\right)}ln_e\left\{\frac{T_1-t_1}{T_1-t_2+\frac{(T_1-T_2)(t_1-t_2)}{(t_2-t_1)}}\right\} \quad . \quad . \quad (k)$$

$$(\Delta t)_{av}=\frac{(T_1-t_1)-(T_2-t_2)}{ln_e\left(\frac{T_1-t_2}{T_2-t_2}\right)}=\frac{\Delta t_1-\Delta t_2}{2.3\ log_{10}\left(\frac{\Delta t_1}{\Delta t_2}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (l)$$

BASIC EQUATION FOR CONDUCTION THROUGH A HOMOGENEOUS BODY

In the preceding pages all problems considered fall under one of two special cases: (a) where the temperature varies only with the location of the point, and (b) where the temperature is a function of time alone.

Wherever the temperature gradient varies with *both* time and the location of the point, one must resort to the general basic differential equation for the conduction of heat through a homogeneous body:

$$\left(\frac{\partial t}{\partial \theta}=\frac{k}{\rho C}\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right).\right.$$

Here x, y, and z are the three axes at right angles to each other, ρ is the density in lbs. per cu. ft., C is the specific heat, and t, θ, and k are as previously defined, namely, degrees Fahr., hours, and B.t.u. per ft. per degree Fahr. per hour. The ratio $k/\rho C$, whose numerical value depends on the physical properties of the body, is called the "thermal diffusivity." For convenience in integration, this ratio is often called α^2.

For certain definite shapes and boundary conditions, this equation may be integrated, although the resulting equations are complicated. However, by arranging the variables of the integrated equations in dimensionless groups, and by plotting the functions, one obtains curves which may easily be used for the solution of practical problems. For example, Gurney and Lurie[1] have published such curves applicable to the batch warming and cooling of spheres, cylinders, slabs, etc., together with illustrative problems. The use of these curves involves the numerical values of "surface emissivity," or h_c+h_r, such as given on pp. 168–169.

[1] Ind. Eng. Chem., Vol. 15, No. 11, p. 1170 (Nov., 1923).

CHAPTER V

FUELS AND POWER

THE commercially important *sources* of energy are fuels and water power; the commercially important *forms* of energy are heat, mechanical energy, and electrical energy. The energy content of fuels is always first transformed into heat energy which may be utilized directly, or transformed into mechanical energy by the use of either the steam engine or the internal combustion engine. The mechanical energy may again be transformed into electrical energy and then finally into either chemical energy or heat. The utilization of water power is always carried out through the production of mechanical energy which may then be transformed into electrical or heat energy if desired.

FUELS

The basis of the commercially important fuels is carbon and its compounds with hydrogen. They are classified, first into primary or natural fuels, such as wood, lignite, coal, crude petroleum and natural gas, and second, into secondary or prepared fuels, such as charcoal, coke, fuel oil, water gas and producer gas. A second classification frequently met, although of minor importance, is based upon whether the fuel considered be solid, liquid or gaseous. The natural fuels have similar origin and represent progressive stages of the transformation which vegetable matter slowly undergoes when protected from complete oxidation.

Upon ultimate analysis these fuels are found to contain carbon, hydrogen, sulphur, nitrogen, oxygen, and ash, the mineral constituents (other than sulphur) being grouped together under the last head. It is not definitely known how these elements are

combined, but it is convenient for purposes of calculation to arrange the analytical results as follows:

1. Moisture (loss in weight at 100° C.),
2. Combined water,
3. Carbon,
4. Free hydrogen (other than that in moisture and combined water),
5. Sulphur, nitrogen, etc., in small amounts,
6. Ash.

In fuel calculations the sulphur and nitrogen are often neglected, though usually present in amounts from 1 to 3 per cent. Since the hydrogen content is always in excess of that necessary to form water with the oxygen, it is often assumed for purposes of calculation and comparison that all the oxygen is in the form of water of chemical combination, and the excess of hydrogen may be termed "free" or "net" hydrogen. The carbon content of coals increases and the percentage of oxygen (or combined water) decreases in the following order: lignites, brown, subbituminous, bituminous, and anthracite coals.

The usual approximate method of expressing the composition of a fuel is to assume it to consist of moisture, combustible matter and ash. Upon ignition in the absence of air under specified conditions of time and temperature (covered platinum crucible) the fuels lose all of the combined water and hydrogen and a large proportion of carbon in the form of volatile hydrocarbons, leaving the ash and the residual carbon. This loss upon ignition is called "volatile combustible matter." The combustible left after this ignition is called "fixed carbon." The ash is the residue left from the complete combustion of the sample in the open air, the sum of moisture, volatile combustible matter, fixed carbon and ash being 100 per cent. The coals mentioned above decrease in content of volatile combustible matter in the order named.

The ultimate analysis of coal is difficult and is often omitted. Bureau of Mines Bulletin No. 29 contains the analyses of coals from practically all American fields of importance. Where the origin of the coal in question is known, it is usually safe to assume the ultimate analysis of its *combustible matter* identical with that given for the same field. The same bulletin shows that the heating value of a coal is within narrow limits a function of the ratio

of its carbon content to oxygen plus ash. The curve given in that bulletin can be satisfactorily represented by the following equation,

$$\text{B.t.u.} = 16{,}750 - \frac{17{,}230}{r + 0.98},$$

or

$$r = \frac{17{,}230}{16{,}750 - \text{B.t.u.}} - 0.98.$$

r is the ratio of carbon to oxygen plus ash. The equation may be applied to a coal on either a wet or dry basis and is often useful in estimating the carbon content of a coal.

Comparison of the Commercial Sources of Mechanical Energy.—The commercially important primary sources of mechanical energy are water power, and solid, liquid, and gaseous fuels. The two latter are capable of direct utilization for the production of mechanical energy in internal combustion engines with an energy efficiency as high as 20 or 25 per cent. On the other hand, the price of liquid and gaseous fuels is excessive except in certain localities, and their use for industrial work is usually restricted on this account. Furthermore internal combustion engines have certain disadvantages which will be pointed out on page 192. As a result relatively small amounts of commercial power are developed from primary liquid and gaseous fuels.

The major commercial sources of mechanical energy are therefore water power and solid fuels. The energy of the latter can be obtained in mechanical form either by the use of the steam engine or the internal combustion engine, and a comparison of water power with the two latter is therefore essential.

The energy utilized by harnessing water costs nothing directly, and it is therefore frequently assumed that water power must in consequence be cheap. As a matter of fact, while water power is the source of the cheapest mechanical energy known, the conditions where such cheap energy is available from water are relatively rare and very frequently water power fails to compete with fuel power. Water power is cheap where a large storage supply is available, insuring constancy of flow throughout the year, where the mechanical development can be made at small expense by the construction of a relatively small dam with short transportation of the water to the wheels, where the expense of costly water rights is not involved, and where effective industrial utilization of the power is possible at the point of generation.

If constancy of flow throughout the year is not assured, it is necessary to shut down the industrial plants depending upon this power when water is low or else to provide a fuel plant capable of handling the load. This involves an investment for a fuel plant which will lie idle a large fraction of the year. The mechanical development of a water power is often very expensive where proper foundations are not available and large dams and expensive penstocks are required. Most especially is it true that water rights are likely to tie up very large amounts of capital and finally while modern high-tension distribution is relatively efficient from an energy point of view, it is none the less expensive in money cost. So rarely does a water power meet all of these requirements that the cases where water power can compete with fuel are surprisingly few.

Since large scale distribution of power is usually electrical, power costs are generally quoted in electrical units. The cheapest powers known are certain developments in Scandinavia, Iceland, and Canada, costing from \$3.50 to \$5.00 per kilowatt year [1] at the generating switchboard. Niagara Power probably costs under \$10.00, though on account of the demand in the immediate district, it cannot be bought for that figure. Through the rest of the United States \$20.00 to \$25.00 represents an extremely cheap water power, and such figures can be realized only in large installations; \$40.00 to \$60.00 may be taken as normal for powers of moderate size, and \$75.00 is rarely exceeded.[2]

Where fuel is to be transformed into mechanical energy a choice must be made between the two methods of transformation, *i.e.*, between the steam engine or turbine and the internal combustion engine. For the use of the latter, solid fuel must be gasified by one of the methods given above, almost always by the generation of producer gas. The steam turbine will under the best conditions give a thermal efficiency of over 20 per cent, but

[1] Note that this is a unit of *energy*.

[2] No commodity sold commercially varies more in selling price than electrical energy. It is available in quantity in Norway at less than a twentieth of a cent a Kw.-H. It is sold to householders as lighting power at around ten cents, two hundred times as much. The sale of it in the form of dry cells is an important industry and in this form the price is over ten dollars per Kw.-H. Thus the variation in market price of it is over twenty thousand fold. The fact of the matter is that the commodity sought is not so much energy itself as that factor which the power engineer calls "readiness to serve."

from 10 to 15 per cent is very satisfactory. On the other hand, the internal combustion engine will, under the best conditions, give a fuel efficiency of over 25 per cent and 20 per cent is not infrequently realized. This being the case, it would at first seem that the steam engine or turbine cannot possibly compete with the gas engine. This is, however, by no means true. In the first place, for a given output the investment in a gas engine plant is much greater than in a steam engine plant. In the second place, a gas engine plant possesses very little overload capacity, because neither the gas producer nor the gas engine can be forced much beyond its normal rating; while on the other hand, the steam engine plant, both the boiler and the engine, is capable of overloads even exceeding 200 per cent. Furthermore, for moderate overloads the efficiency of the steam engine plant does not very greatly decrease. Inasmuch as a plant must be designed for its maximum load, this means that in any plant subject to occasional excessive overloads the investment required for a gas engine plant is very much larger than that necessary for a steam plant. Again, the wear and tear and consequently the depreciation in a gas engine plant is a heavier expense than in a steam engine plant. Finally, the internal combustion engine is unsuited for use as a prime mover for electrical generation on account of the speed fluctuations due to the variations in the power impulse. While this difficulty can be and has been to no small degree overcome, it is none the less a disadvantage under which the gas engine plant labors. Against all these disadvantages is the single advantage of fuel economy, and the result is that the gas engine is utilized as a prime mover where fuel is high or load conditions unusually uniform, but where fuel is relatively cheap and loads fluctuate it is unable to compete with steam generation. In exceptional cases, however, where large amounts of cheap gas are available, as in the steel industry, gas engines are used extensively.

CHAPTER VI

COMBUSTION

Fuels are substances capable of combining with oxygen with evolution of heat, and their utilization for energy production almost always involves a reaction with air. All combustion reactions are therefore gas reactions, and the characteristics of all gas reactions apply to them and control combustion processes. The major reactions involved are

1. $C+O_2 = CO_2+97{,}000$ cal.
2. $CO_2+C = 2CO-39{,}000$ cal.
3. $2C+O_2 = 2CO+58{,}000$ cal.
4. $2CO+O_2 = 2CO_2+136{,}000$ cal.
5. $2H_2+O_2 = 2H_2O+136{,}600$ cal.
6. $H_2O+C = CO+H_2-39{,}300$ cal.
7. $2H_2O+C = CO_2+2H_2-39{,}600$ cal.
8. $CO+H_2O = CO_2+H_2-300$ cal.

The heat quantities quoted apply to the combination of the number of gram mols of reacting substances indicated on the left-hand side of each equation, at room temperature (20° C.), at constant pressure and with *liquid* water (*i.e.*, water condensed if formed and evaporated if used). The reaction heats change with the temperature, the change being calculable from the specific heats of the reacting substances.

The following facts must constantly be kept in mind in regard to all combustion processes.

1. Equilibria. *All of these reactions are reversible.*—In the case of any reversible reaction which liberates heat, equilibrium is displaced backwards by a rise in temperature (Principle of Le Chatelier). The first reaction, it is true, does not reverse directly, but CO_2 breaks down first into CO and O_2 by the reversal of the fourth reaction. This dissociation of CO_2 is scarcely measurable below 1400 or 1500° C., but above this temperature it increases. Carbon monoxide decomposes into carbon and oxygen by the

reversal of the third reaction, beginning at approximately 2500° C. and increasing with the temperature.[1] The point at which this reaction is greatly reversed is not, however, known. The combination of the reversal of Reactions 4 and 3 accomplishes the reversal of Reaction 1. Reaction 2 goes to the right only at high temperatures, nearly quantitatively above 1000° C., but rapidly reversing below that temperature so that at 500° C. it is almost quantitatively reversed. In other words, above 1000° C. only carbon monoxide can exist in appreciable amounts at equilibrium in the presence of carbon, the fraction of carbon dioxide being very small, while at low temperatures carbon is incapable of reducing carbon dioxide to carbon monoxide except to a slight extent. Reaction 5 begins to reverse appreciably at about 1300° C. and at 1600° or 1700° the reversal is distinct. Neither the sixth nor seventh reaction is complete nor can it take place by itself alone, but in the presence of water and carbon the CO and CO_2 produced by both of these reactions interact with the excess carbon according to Reaction 2. Reaction 8 is important in the production of secondary gaseous fuels. The conclusions of G. N. Lewis and Randall[2] as to the equilibrium constants of these reactions as functions of the temperature, based on a critical survey of all data in the literature, are shown in Fig. 46. These curves correspond to equilibrium with carbon in the form of *graphite.*

[1] This stability of CO is one of the important reasons for the value of the oxy-acetylene flame. Acetylene is very rich in carbon, and, if burned with enough oxygen to form CO only, gives reaction products stable up to 2500° C. Were more oxygen used much more heat would be set free *at low temperatures,* but above 1500 to 1800° the CO_2 and H_2O formed would dissociate, reabsorbing the heat evolved by their formation, and serve as diluents to keep down the reaction temperature. While, therefore, the production of CO evolves less heat, it is available at a much higher temperature. Fortunately, too, acetylene has a negative heat of formation from the elements, carbon and hydrogen, and upon combustion this is available in addition to the heat of formation of CO, thereby increasing the heat effect. Furthermore, the flame produced under these conditions, consisting mainly of CO and H_2, is strongly reducing in character, so that metals heated with it are protected from oxidation. This is because the affinity of carbon for oxygen (to form CO, though not to form CO_2) is so much greater than the affinity of most of the metals for oxygen. Finally, the affinity of carbon for oxygen is also so much greater than that of the metals for carbon, that very little carbon is absorbed by the metal from the flame, thus avoiding the brittleness and other evils resulting from the formation of metallic carbides.

[2] *J. Am. Chem. Soc.,* **36,** 1969–1993 (1914), and **37,** 458–170 (1915).

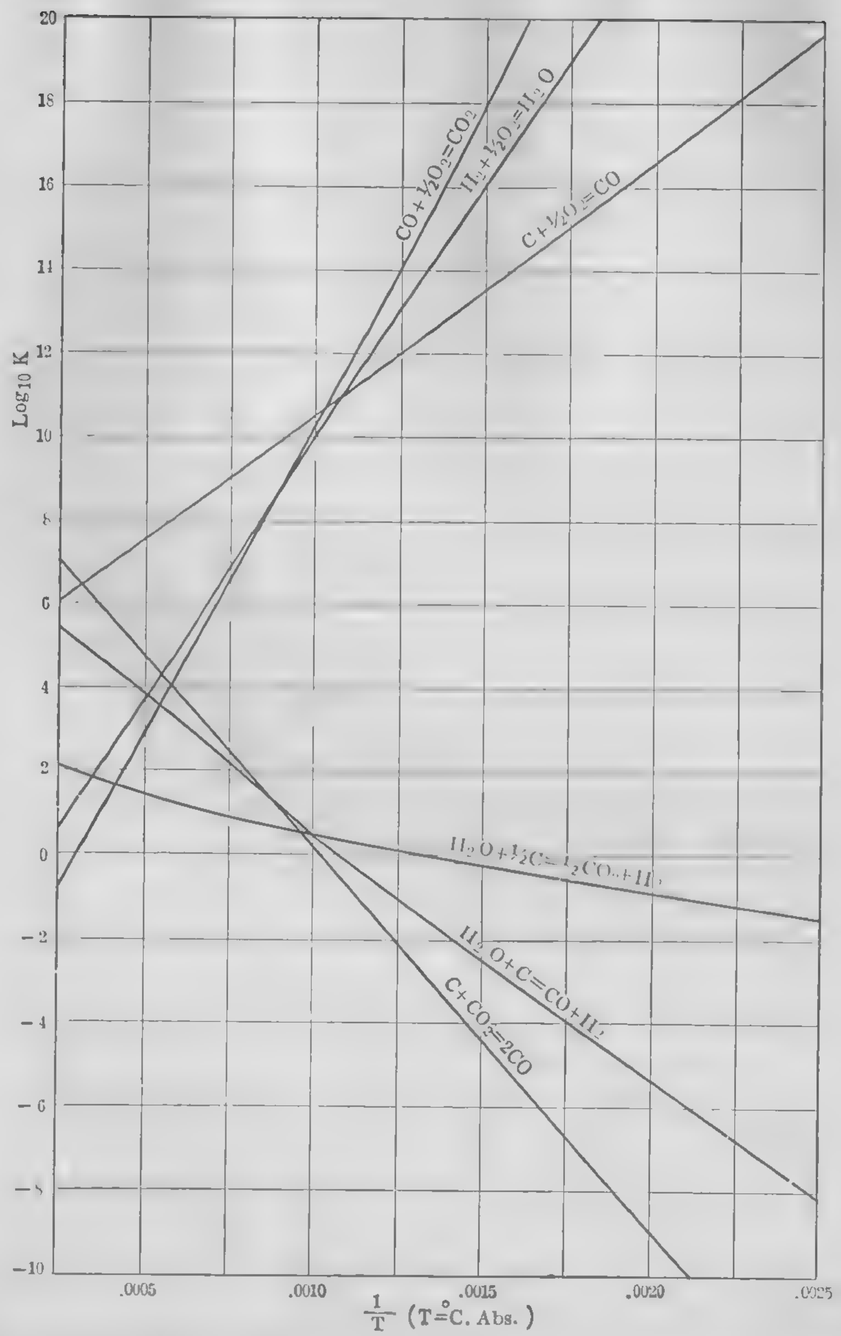


FIG. 46.—Equilibrium Constants, K, of Combustion Reactions, *Carbon as Graphite.*

These constants are in terms of partial pressures, expressed in atmospheres. They are based on the equations as written on the chart. Thus for the reaction, $C + \frac{1}{2}O_2 = CO$, at $1/T = 0.002$, $\log_{10} Kp = 16.6$, or $K_p = 4.10^{16}$, where $K_p = p_{CO}/\sqrt{p_{O_2}}$

2. Specific Reaction Rates. *The rates at which these reactions proceed are of vital importance.*—All gas reactions are relatively slow, but some are much more rapid than others. Reaction 1 is extremely rapid at high temperatures (above 800° C.); reaction 2 is slow and negligible in comparison with 1 at combustion temperatures, though not below 600° C. All three of these reactions involve an interaction of a gas with solid carbon and therefore, other things being equal, the rates are proportional to the surface of carbon exposed. On the other hand, carbon is characterized by the fact that it changes its condition upon prolonged heating, assuming denser and more compact forms. The less dense forms of carbon react with gases far more rapidly than the more compact sorts. Thus, charcoal and the carbon from soft coal react extremely rapidly, whereas coke, especially if burned at high temperature, and anthracite coal are relatively very slow. This applies to the interaction of all gases with these different forms of carbon. Reactions 4 and 5 are purely gas reactions, but are relatively slow. The data indicate that 5 is approximately four times as fast as 4. Reactions 6 and 7 again involve interaction of a gas with solid carbon, and the influence of the form of carbon upon the rate is similar to that in the first three reactions. The bases for these generalizations will appear later.

3. Contact Catalysis.—*All gas reactions are greatly increased in rate by contact with hot surfaces, i.e.,* hot surfaces act as catalysts of gas reactions. It is, of course, well known that specific bodies, *e.g.,* platinum, nickel, etc., act as specific catalysts for certain reactions, but it is equally true that all hot bodies catalyse gas reactions to a marked degree. Gas reactions which take place very slowly indeed in the interior of a large mass of gas proceed much more rapidly on the surface of that mass where the gas is in contact with the hot walls of the container.[1] To accelerate gas reactions it is therefore merely necessary to bring the reacting gases into contact with hot bodies. Thus Reaction 8 is capable of catalysis by hot carbon independently of interaction with it.

4. Temperature Effect. *Gas reactions,* as with all chemical reactions, *are greatly accelerated by rise in temperature,* and the degree of acceleration is nearly the same for all reactions. The

[1] This experimental difficulty is the reason for the lack of data on rates of gas reactions at high temperatures.

rate approximately doubles for every 10° C. at ordinary temperatures but this rate of increase falls off greatly at high temperatures. Thus at 1000° C. it requires an increase of roughly 100° to double the rate. It is impossible, however, to accelerate any one chemical reaction by rise in temperature without at the same time accelerating all other reactions which are possible under the conditions involved.

5. Interactions of Solids and Gases.—In order for the combustion of a solid fuel to proceed at a rate practicable for the industrial generation of heat the fuel must be raised to a relatively high temperature—at the very least 700° to 800° C. Before such a temperature is reached the volatile constituents of the fuel are almost completely distilled[1] out, so that the *combustion* of the solid fuel is that of carbon itself (coke or charcoal). It should, however, be noted that the gaseous distillation products may burn long before combustion of the solid residue starts.

When coal distills as it is being heated to incandescence it evolves hydrocarbons which upon further heating themselves thermally decompose ("crack") with deposition of extremely finely divided carbon (smoke, soot). This carbon once formed is swept away in suspension in the gases to zones in the furnace where oxygen concentration is low (and where, as will appear later, it is very desirable to keep it low) and it is consequently very difficult to burn. Fortunately, however, its formation in the first place can be prevented by taking advantage of the observation of Bone[2] that these hydrocarbons, which are formed at temperatures below their ignition point, if heated mixed with oxygen combine with it, not burning to CO or CO_2, but forming addition products which on thermal decomposition deposit no carbon. The affinity of carbon for oxygen to form CO is so great, that if

[1] The volatilization of material from relatively non-volatile organic substances by the process of thermal decomposition at high temperatures is called *destructive distillation.*

In the case of liquid hydrocarbons the thermal decomposition itself is called *cracking,* whether or not associated with volatilization. The phenomenon must not be confused with ordinary distillation, which takes place without chemical decomposition (see Chap. XVII, p. 558).

Whenever the term *distillation* is employed in this and the next two succeeding chapters, it refers to destructive and not ordinary distillation.

[2] Bone, *J. Chem. Soc.,* **83,** 1074 (1903) and **85,** 693 (1904).

oxygen be present in the molecule it will combine with any carbon which might otherwise be formed on further heating. Hence to prevent smoke formation it is necessary only to coke the coal in a stream of air. This is especially important in the case of the high-grade (high heating value), high-volatile bituminous coals. In the case of the lignites and brown coal the volatile matter, though large in amount, is so rich in oxygen (combined water) that carbon formation is less. The smoke from these coals is easier to burn, but unfortunately the furnace temperatures realized are so low that this advantage is largely counterbalanced by the consequent lower reaction rate.

In high-grade bituminous or anthracite coals the heat absorbed by this distillation is a small fraction of the total heat evolved upon combustion, but fuels containing large quantities of water, either free or combined (lignites, brown coals, etc.) consume a great deal. This heat absorption chills the furnace and accordingly interferes with combustion.

Solid fuels may be burnt in two ways; supported upon a grate designed to admit the air necessary for combustion, or finely divided fuel (powdered coal, sawdust or shavings) may be blown into the furnace in such a way that each particle passes through the combustion space along with and surrounded by the air requisite for its own complete combustion. The former is the more usual method, and because a study of this type of combustion well illustrates the underlying facts and principles, it will be considered in detail here.

Primary Combustion.—Consider a grate upon which rests a bed of coke formed by the distillation of the coal. Through this hot coke rises a stream of air, which supports its combustion. If one samples and analyzes the gases at various points in this fuel bed, and plots the gas analyses as ordinates against the height of the point of sampling above the level of the grate bars, as abscissæ, one obtains curves similar to Fig. 47. These curves will vary somewhat with the character of the coal, with its size and with the air velocity. However, wide variations in these controlling conditions cause relatively small changes in the curves, especially in their positions relative to each other. Thus the percentage of oxygen has usually fallen to 2 or 3 per cent within 2 to 4 in. above the grate.

The temperature in the fuel bed is surprisingly uniform. It is of course low at the grate because of the cooling effect of the entering air. It rises at first sharply and then gradually to a maximum a few inches below the upper surface of the fuel bed and then decreases slightly. Obviously, the combustion reactions cannot progress until the temperature has reached the ignition point, 600 to 800° C. Although the cold air entering the fuel bed through the grate bars chills the mass at this point, heat flows down through the fuel bed at a very high rate by both conduction and radiation. Furthermore, the instant ignition starts, reaction is so rapid, owing to the high concentration of oxygen, that heat generation at the bottom of the fuel bed is very great. In the case of petroleum coke (very low in ash) these factors keep the temperature at the bottom of the bed so high that it is almost impossible to avoid burning the grate bars. However, with coal and ordinary coke the residual ash protects the grate bars and dilutes the combustible to such an extent that the temperature rise above the grate bars is less sharp. It is general practice in

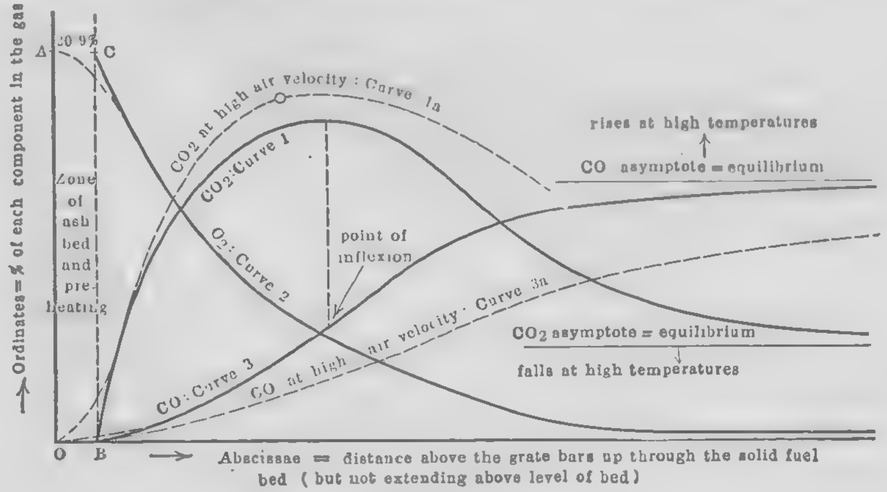

Ordinates = % of each component in the gas
A
20.9%
C
Zone of ash bed and pre-heating
CO_2 at high air velocity : Curve 1a
CO_2: Curve 1
O_2: Curve 2
CO: Curve 3
CO at high air velocity: Curve 3a
point of inflexion
rises at high temperatures
CO asymptote = equilibrium
CO_2 asymptote = equilibrium
falls at high temperatures
O
B
Abscissae = distance above the grate bars up through the solid fuel bed (but not extending above level of bed)

FIG. 47*.

burning petroleum coke to use enough coal to form and maintain a protective bed of ashes on the grate.

Owing to these effects the combustion reactions do not ordinarily start sharply at the grate bars but a little above them. In Fig. 47 [1] the curves starting along the line *BC* are those obtained

[1] Based on data of KREISINGER, OVITZ, and AUGUSTINE, U. S. Bureau of Mines, Tech. Paper 137 (1917).

in the burning of petroleum coke without admixed coal, while the curves starting along the line *AO* are the normal type. It will be noted that the two sets of curves become identical a short distance above the grate bars. Because of the absence of complication due to ash, discussion will be limited to the curves starting from *BC*. Where ash is present, the line *BC* may be called the effective position of the grate bars.

For a given coke—whether fired as such or produced on the grate itself by the distillation of the coal—of a given lump size or size distribution (*i.e.*, screen analysis), the O_2-curve and the early part of the CO_2-curve both remain practically unchanged [1] whatever the air velocity through the fuel bed. Also, at the start each is symmetrical with respect to the other, the CO_2-curve plotted up being identical with the O_2-curve plotted down from the initial oxygen content of the entering air, 20.9 per cent. Furthermore, in this region each is a logarithmic curve, *i.e.*, the CO_2-curve is a straight line if plotted directly on semi-logarithmic paper, as is also the case if 20.9 minus the O_2 content be so plotted.

These facts demonstrate that rate of oxygen disappearance and carbon dioxide formation are equal and each proportional to the oxygen content of the gas at a given point in the fuel bed, *i.e.*, that the primary reaction in the combustion of carbon in air is $C+O_2=CO_2$, and this reaction is monomolecular with regard to O_2. Furthermore the fact that these curves do not change with increasing air velocity, despite the accompanying increase in temperature due to increased heat evolution, indicates that the rate of combustion is controlled, not by the rate of chemical combination on the surface of the carbon, but by the rate of diffusion of the oxygen through the surface film of air around each carbon particle (see p. 36). Doubling the air velocity approximately halves the thickness of this film. Consequently with the same gradient in oxygen concentration twice as much oxygen diffuses into the surface of the carbon where, at the temperatures of the fuel bed, its combination with the carbon is practically instantaneous. The CO_2 now diffuses out against the oxygen diffusing in.

Change of diffusion velocity with temperature is small within the range involved. One might assume that the rise in temperature with higher air velocity increases the reaction rate just sufficiently to keep the rate of CO_2 formation proportional to velocity,

[1] Within the experimental error, which is admittedly large.

but such exact adjustment of temperature to velocity under the widely varying conditions of heat dissipation seems out of the question. The above facts are compatible with the assumption of CO as the primary product of oxidation, this being oxidized to CO_2 as it diffuses through the air film, but the simultaneous presence of O_2 and CO further above the grate demonstrates that the rate of combustion of these two is not sufficient to explain the absence of CO at the bottom of the fuel bed. CO_2 is therefore the primary product of combustion.

The CO curve starts out asymptotic to the horizontal axis, and its slope is at all points roughly proportional to the CO_2 content of the gases. It is, however, much flatter than the two preceding curves. At its right-hand end (after O_2 has disappeared) it becomes symmetrical with the CO_2 curve with respect to two horizontal asymptotes corresponding to the equilibrium between CO_2, CO and carbon. If air velocity be increased, the CO curve and the right-hand end of the CO_2 curve both flatten and move to the right, but the displacement to the right is much less than proportional to the velocity. These facts signify that CO is formed by the reaction, $CO_2+C=2CO$; that the rate of this reaction is controlled—not by gas diffusion through the gas film around the carbon particles—but by the rate of chemical interaction of CO_2 and carbon; that with the increasing temperature corresponding to increasing air velocity the reaction rate increases, but less rapidly than the air supply; and finally that, even at high temperatures, this reaction is much slower than the formation of CO_2 from O_2, so that equilibrium is approached only with very deep fuel beds and long time of contact of gas and carbon.

It is obviously impossible to operate a fire properly with too thin a fuel bed. It must be at the very least 3 to 6 in. deep to avoid chimneys and thin spots which render proper control out of the question, and it is usually wiser to use much thicker beds. Inspection of these curves shows that the gases leaving the bed carry little or no oxygen, but do contain monoxide, which represents incompletely burnt fuel. It is therefore necessary to mix additional air with the gases leaving the fuel bed and to give opportunity for oxidation of this monoxide, of any hydrogen formed by decomposition of water vapor in the air or left in the coke and of the hydrocarbons formed by initial distillation of the coal. The reactions in the fuel bed itself are spoken of as *primary com-*

bustion, while the burning of the gaseous products evolved is called *secondary combustion*.

Producer Gas.—Gaseous fuels are relatively clean and free from ash, and, mainly because of the limited amount of fuel in the furnace at any one instant, admit of exact control of temperature and heat supply. Of the secondary gaseous fuels, coal gas has the highest heating value and is therefore the easiest to distribute, but its cost is too high for most industrial furnaces. Hard coal or coke can be gasified by decomposition with steam (water gas) but this reaction absorbs heat which has to be supplied by alternately blowing with air. Mere primary combustion of a solid fuel with a thick fuel bed obviously yields combustible gas and this method is sometimes used, but the fuel bed gets very hot at the bottom (where the coke is burning almost quantitatively to CO_2) resulting in trouble from fusion of the ash. One may, however, introduce steam (or occasionally CO_2 in the form of flue gas) with the air, thus absorbing the excess heat by its interaction with the coal, yielding *producer gas*. This may be used directly as hot, raw producer gas, or it may be cooled and purified. Raw gas can only be used in a furnace directly connected with the producer. Because of the simplicity of its production and its cheapness, producer gas is widely used and its importance is increasing. Its main disadvantage is its low heating value, due to the diluent nitrogen from the air, but this can be largely overcome by the use of proper preheating and heat recovery devices (see p. 228).

Since producer gas is formed by the interaction of steam and carbon superimposed upon primary combustion with air, especial attention must be paid to the steam reactions. It is found that if the reaction products of *steam alone* be plotted as shown in Fig. 48 the curves obtained are the same whatever the character (fineness, porosity, etc.) of the carbon [1] or the pressure of the steam or the time of contact of steam with carbon. Furthermore, temperature has only a slight influence. All these variables, however, profoundly affect the extent to which the decomposition goes in a given time.

As just stated, change in pressure of the steam used does not affect these curves. It will be noted, however, that the curves are so plotted as to eliminate as a variable time of contact of the

[1] Except that wood charcoal gives entirely different results, with higher CO_2.

steam with the carbon. The experimental results also show that the time required to get the same identical effect, other things being equal, is inversely proportional to the pressure. These facts demonstrate, first, that if water-vapor takes part in more

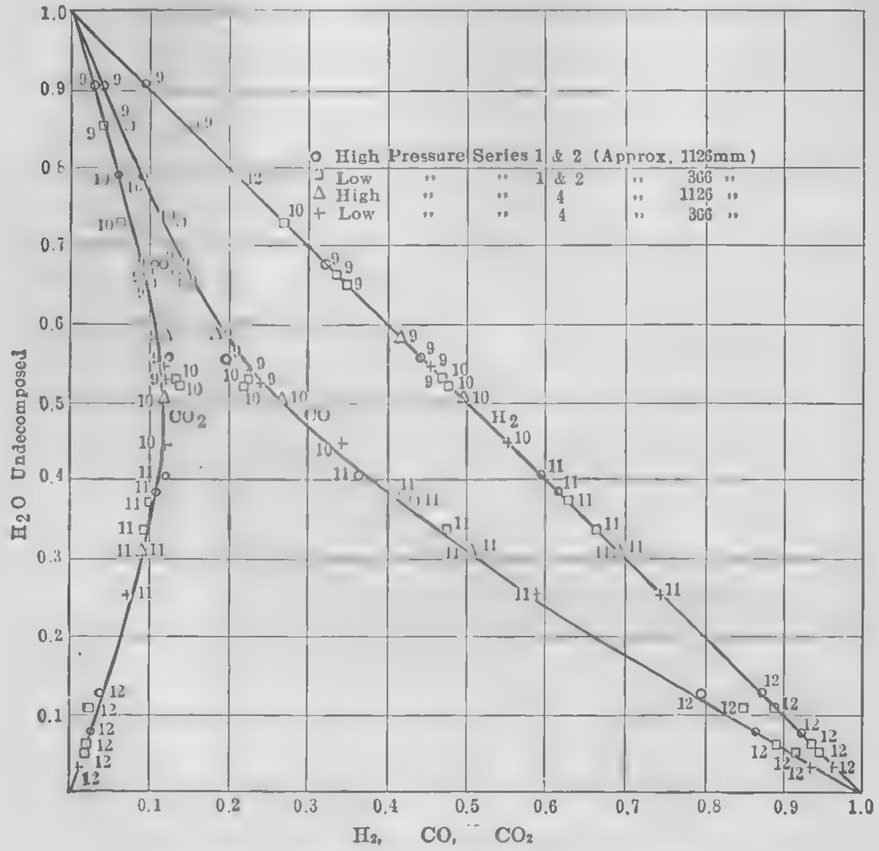


FIG. 48.—Water-gas Formation. (*Bases for Ordinates and Abscissas is H_2O+H_2; Numerals Represent Centigrade Temperature in Hundreds of Degrees.*)

Haslam, Hitchcock, and Rudow, J. Ind. Eng. Chem., **15**, *No.* 2, *1923.*

than one reaction the order of each of these reactions must be the same with respect to it, since otherwise change in pressure would change the rate of one reaction more than another and therefore throw the net results off the curve; and second, that all these reactions must be monomolecular with respect to water, since otherwise the influence of pressure could not be proportional to the effect of time. It will be noted that the CO_2 and CO curves

both have finite slopes at the start. This means that both these gases are produced simultaneously by the *primary* reactions between steam and carbon. This can be explained only on the assumption that the two primary reactions are those given as 6 and 7, page 193:

6. $H_2O+C = H_2+CO$.
7. $2H_2O+C = 2H_2+CO_2$.

The second reaction must, however, be monomolecular with respect to water as indicated above. This means that the mechanism of this reaction is unknown.

Since these reactions are found to be independent of the amount of carbon surface exposed, the influence of carbon on all reactions taking place simultaneously must be the same. Indeed study of the data shows that time, pressure and surface are substantially equivalent to each other in their effect; *i.e.*, if one doubles the surface at constant pressure one halves the time required to secure the same results, etc.

These curves can be represented quantitatively with reasonable precision by assuming the following three simultaneous reactions, the reaction rates being k_6, k_7, and k_2 respectively, and the ratios of these reaction rates being substantially constant from 1,000 to 1,200° C., the approximate temperature range in which they are commercially used.

6. $H_2O+C \rightarrow H_2+CO$.
7. $2H_2O+C \rightarrow 2H_2+CO_2$.
2. $CO_2+C \rightarrow 2CO$.

The usual reaction rate equations are most conveniently set up by assuming one part of entering steam or, what is equivalent to the same thing, a basis of H_2O+H_2 in the gas, since this is constant. On this basis call the residual water remaining undecomposed, x, the CO_2, v, and the time θ. Therefore, the rate of disappearance of water is

$$-dx/d\theta=(k_6+2k_7)x$$

and the rate of formation of CO_2 is

$$dv/d\theta=k_7x-k_2v,$$

whence

$$dv/dx=\frac{\beta v-x}{\alpha x},$$

where

$$\beta=k_2/k_7 \text{ and } \alpha=2+(k_6/k_7).$$

The solution of this equation is

$$(\beta-\alpha)v=x-x^{\beta/\alpha}.$$

For the curves of Fig. 48,

$$\beta=4.18,\ \alpha=3.17,$$

whence

$$1.01v=x-x^{1.319}$$

For the use of these equations, see page 260.

It is interesting to note that the final products of interaction, unless the time of contact be very great indeed (this is not shown on the curves), are dictated by relative reaction rates rather than equilibria.

These curves do not, however, tell the story of reaction rates, which increase with temperature and carbon surface. Below 800° C. they are very slow. In the neighborhood of 1000° C. these reactions approximately double in rate for each 100° rise in temperature, but the temperature increment required to double the rate steadily increases with the temperature (roughly inversely proportionally to the square of the absolute temperature). In producer gas practice the temperature is kept as high as possible without fusion of the ash in order to keep up reaction rate and secure maximum capacity from the apparatus.

In producer practice Reactions 1 and 6 start simultaneously. Reaction 8 plays almost no part, going to the left if at all, because there is at the start but little H_2 to reduce to CO_2 and at the end but little steam to oxidize the CO. Reaction 1 quickly completes itself, after which 6 and 2 go hand in hand, 6 being much the more rapid.

6. Combustion of Liquids.—All combustible liquids volatilize largely if not wholly before reaching combustion temperature, many of them decomposing thermally (cracking) rather than vaporizing unchanged. Those which readily vaporize without decomposition may be mixed with air before ignition as in internal combustion engines but in furnace practice the liquid is usually broken up by atomization into an exceedingly fine spray mixed with the air necessary for its own combustion. Under these conditions the processes of distillation, cracking, primary and secondary combustion take place almost simultaneously. Because of the large surface exposed the combustion rate is extremely high and

because of the small amount of fuel in the combustion zone at any one instant control is excellent.

7. Combustion of Gases.—As already stated the rate of oxidation of all the combustible gases is slow except at very high temperatures and in sufficiently high concentration of the gases and oxygen. Where the concentration of the gas and oxygen is such that combustion following ignition at one point generates enough heat to raise the neighboring portions of the mixture to ignition temperature, it is obvious that a flame once started will propagate itself with great rapidity. This point constitutes the lower explosive limit. If the amount of combustible gas be increased sufficiently it will itself finally act as a diluent sufficient to prevent combustion, thus determining the upper explosive limit.

In furnace practice the first problem of combustion is complete mixing of the gas and air and the next is the provision of sufficient time for the combustion reactions to complete themselves. These will be discussed in Chapter VII.

It has already been pointed out that hot surfaces serve as catalysts for all gas reactions. It is therefore highly desirable to bring the gases into intimate contact with hot refractory surfaces in order to complete combustion in the least possible time. That combustion by catalysis may be of controlling importance is shown by the fact that at low temperatures the combustion of mixtures of hydrogen and oxygen is proportional, not to the time of exposure of the gases to combustion temperatures, but to the surface of the container. That the mechanism of combustion by surface catalysis is entirely different than that of oxidation in the gaseous phase is demonstrated by the experimentally determined fact that whereas the combustion of hydrogen catalytically is monomolecular with respect to hydrogen, combustion in the gaseous phase is dimolecular. Quantitatively very little is known concerning the specific reaction rates or the influence of the character of catalytic surfaces upon them.

CHAPTER VII

FURNACES AND KILNS

In order to utilize to the greatest advantage the heat energy made available by combustion, it must be set free in an enclosed space made of fire brick or other heat resistant material, known as a furnace, kiln, retort or oven. Although furnace construction was practiced many centuries before the principles of combustion just presented were understood, the design and operation of modern furnaces in accordance with these principles is an important chapter in the economy of chemical engineering.

Furnaces may in general be divided into two classes according to whether first, the heat of combustion be transferred by direct contact from the fuel, flame, or hot gases to the material to be heated, or, second, the heat be transmitted from the combustion space through some containing wall or partition to the charge, the flame and products of combustion being separated completely from the charge by the use of a muffle, retort, still, or other similar container such as segar or crucible. The first type of furnace has the great advantage of cheaper construction, lower cost of maintenance and operation, and more rapid heating and cooling, and is adapted to maintain a higher temperature. The disadvantages are that the charge is contaminated with the flue dust and other products of combustion which are in many cases objectionable, that the treatment of the charge is limited to chemical conditions compatible with satisfactory combustion of the fuel, and even so is subject to changing conditions of oxidation and reduction resulting from unequal firing, and that any product of the reacting mass which is volatile is lost in the large volume of flue gas. On the other hand, the second type, the muffles, retorts, or stills, have the obvious advantage of easy manipulation of the products of the reacting mass, and a more uniform control of the temperature and of the chemical conditions of the atmosphere in the furnace. If the temperature be relatively low and

the containing wall of metal, as in a still, low heat transmission capacity due to poor conductivity is avoided, but in muffles of heavy fire-brick construction the temperature drop through the wall is great and for rapid heating the combustion space must be maintained at a much higher temperature than the interior of the vessel, with consequent loss of heat in the flue gases and low heat efficiency.

In some cases the fuel may be mixed directly with the charge and the most intimate contact obtained between the source of heat and the object to be heated. This advantage finds its most perfect realization in those electric furnaces in which the charge forms its own resistance; such furnaces of course do not use fuel but, as in the case where fuel is mixed with the charge, the heat is greatest at the point where it is to be utilized. However, in order to maintain through the mass a free passage for the air necessary for combustion, either a strong blast must be used, or the charge must remain rigid and lumpy throughout the operation. This type of furnace has, therefore, in the past been limited to such purposes as the blast furnace in metallurgical work, to the old type lime kiln where the fuel was added with limestone, and to brick and pottery firing.

A third special type of furnaces includes those in which the fuel itself is the only charge (beehive coke ovens, charcoal heaps, etc.).

A second classification of furnaces especially useful as a basis for discussion depends upon the character of the fuel:

1. Furnaces using solid fuels (not powdered nor directly admixed with charge),
2. Furnaces using liquid or powdered solid fuel,
3. Furnaces using gaseous fuel,
4. Furnaces using solid (or liquid) fuel directly mixed with charge.

1. FURNACES USING SOLID FUEL ON GRATES, FUEL NOT POWDERED NOR DIRECTLY ADMIXED WITH CHARGE

Furnaces of this type must support the fuel on a grate and carry out primary combustion at that point. Steam boilers are by far the most important illustration of this type and well

exemplify the problems of design, construction and operation, but, as will appear later, most chemical furnaces must diverge sharply from boiler practice in certain regards.

(*a*) *Coking.*—The first problem is to bring the fuel up to incandescence and this involves the coking of the coal which takes place before ignition temperature is reached. This coking must be carried out in a stream of air if smoke is to be avoided (see p. 197). Consequently the coal must *not* be coked by throwing it on the incandescent fuel bed, since the gases rising from this are oxygen-free. The air rising through the cold fuel must, however, not be large in amount, as otherwise it will exceed that necessary for secondary combustion. In the case of a hand-fired grate proper conditions for coking can be maintained by firing the fresh coal on a small area of clean grate bars immediately in front of the fire door, secured by pushing the incandescent fuel back from this area onto the remainder of the fuel bed. This cold fuel is heated by conduction from the incandescent fuel beside it and by radiation from the furnace walls. It distills with an excess of fresh air rising through it, the excess being later available for secondary combustion. When coked it should be pushed with the hoe back upon the rest of the bed and fresh coal again supplied at this point.

This method is effective in preventing smoke formation but it is laborious in that it requires constant attention to the fire, it being necessary to add the coal in successive small quantities at frequent intervals. In consequence it is difficult to get the fireman to use this method, all the more since no recording or even indicating instrument for smoke measurement has been devised, so that there is no check on the operation except when the inspector happens to be looking at the top of the stack. One of the major advantages of mechanical stokers is their solution of this problem. Both the horizontal chain grate and the inclined rocking grate feed the coal slowly and continuously into the furnace, where it cokes with air rising through it. The latter by its motion rolls the coked fuel down over the rest of the fuel bed, keeping this of uniform thickness, a thing the chain grate fails to do. However, both these automatic types have in common with the hand-fired grate (when operated as recommended above) the shortcoming of letting a certain amount of fresh coal fall through the grate bars where it is difficult to avoid losing it with the ash.

The underfed stoker eliminates this difficulty and is peculiarly efficient in the conditions under which it cokes the coal.

(*b*) *Maintenance of Fuel Bed and Removal of Ash.*—The next problem is to maintain a uniform fuel bed and to remove the ash free from unburnt combustible. In a hand-fired furnace, using a coal with non-packing, non-fusing ash this is easily done. The bed is kept uniform by poking, and the ash is worked through the grate by shaking, keeping on the grate, however, a layer of ashes sufficiently thick to completely burn out the carbon. If the ash packs, it chokes the draft and the grates must be kept so well shaken that combustible is sure to be lost with the ashes. Conditions are even worse with a fusing ash since the effort to get the clinkers through the grate works combustible through with it. The horizontal chain grate is poor in this regard as it leaves a thin fuel bed at the end of its travel. If operated to burn out all the combustible it is prone to let through too much air. It is especially unsatisfactory with badly clinkering coals. The inclined grate keeps a very uniform fuel bed but with clinkering ash the grinding of the grates necessary for its removal balls up large amounts of combustible with the fused ash, since the point of grate movement for ash removal is so close to the high temperature zone of the fuel bed. We have observed 50 per cent combustible in the ash from a furnace of this type. The underfed stoker is especially unsatisfactory in separation of ash from combustible.

(*c*) *Combustion Rates.*—As indicated on p. 200, at furnace temperatures the rate of combination of coke with oxygen to form CO_2 is proportional to the air velocity, so that there is no limit to the amount of coal which can be burnt on a given grate surface, provided the draft is sufficient to pull the necessary air through the grate and fuel bed, until an air velocity is reached sufficient to blow the coal off the grate.

As air velocity through the grate increases, the amount of heat evolved by primary combustion increases slightly more than proportionally. No small fraction of this heat is carried away as sensible heat in the gaseous products of primary combustion, and this heat quantity obviously increases with the temperature of those gases. Where, however, there is in the furnace an object to be heated in "sight" of the fuel bed, either directly or by reflection, a great deal of heat flows by radiation from the fuel

bed to this object, especially in the former case. In boiler practice the boiler is at a temperature so low in comparison with that of the fuel bed that a large fraction of the total heat of primary combustion reaches the boiler in this way. Furthermore, since radiation rises as the fourth power of the absolute temperature, almost all of the excess heat evolved in primary combustion with increasing combustion rate goes to the boilers as radiant energy and this requires very little increase in temperature of the fuel bed. However, in many chemical furnaces there is no body with adequate heat absorption capacity available for taking up this radiation and therefore in such cases the temperature of the fuel bed rises rapidly with increase in combustion rate. If not controlled this will result in localized overheating in the furnace, in fusion of the ash and even in burning out of the grate bars. Consequently, chemical furnaces with limited heat absorption capacity in "sight" of the fuel bed must in general be operated at very carefully limited rates of combustion.

Hand-fired boiler furnaces can be operated successfully at combustion rates of 10 to 20 lbs. of coal per sq. ft. of grate area per hr., while mechanical stokers can be forced to 40 or 50 lbs. Indeed, combustion rates of 80 lbs. have been realized but it is impractical to maintain these commercially. In chemical furnaces the combustion rate is, as stated above, limited by the maximum allowable temperature of the furnace, by its heat absorption capacity and by the necessity for uniformity of heat distribution. Not infrequently in such furnaces combustion rates must be held below from 2 to 5 lbs. of coal per sq. ft. of grate area per hr.

So large is the heat radiation from boiler fires that where low-grade fuels, such as wet wood waste, tan bark, lignite, etc. are used it is necessary to construct the furnace so that the boiler cannot "see" the fire, as otherwise the radiation will cool the fire below combustion temperatures. This is done by building the furnaces entirely in front of the boiler and separating the two by a high bridge wall (Dutch oven construction).

This possibility of an almost unlimited combustion rate on the grate, coupled with the direct transmission of most of the heat evolved by radiation to the point required and its almost complete absorption there is the basis of the tremendous overload capacity of boiler furnaces. The main disadvantage of thus

forcing the boiler is slightly lowered efficiency due to imperfect secondary combustion. Modern practice tends to provide adequate space for secondary combustion to meet this need.

(*d*) *Secondary Combustion.*—From the fuel bed there rise the distillation products of the volatile combustible matter of the fuel and the gaseous products of primary combustion rich in carbon monoxide and containing some hydrogen from the moisture in the air. In the former gases there should be some oxygen if the fuel has been properly fired but in the latter there is little or none. The potential heat of combustion of these gases represents a large fraction of the heat content of the fuels and adequate provision must be made for their oxidation.

The first problem is to mix these gases with the proper amount of air. So great is their volume (owing to the large amount of nitrogen) that complete mixing is difficult to secure. In hand-fired furnaces the secondary air (*i.e.*, this air necessary for secondary combustion) is admitted through dampers in the fire door and mixes with the gaseous products of primary combustion as it sweeps over the fuel bed. In the case of chain and inclined grates no small fraction of the secondary air enters through the distilling fuel. In underfed stokers none whatever comes in this way. In stoker-fired boiler furnaces modern practice is developing toward the admission of secondary air through multiple ports in the bridge wall, the air being preheated during its passage through the flues in the wall which conduct it to these ports. In this way it is possible to admit the air at a large number of points thus improving mixing conditions. The preheating is, as will appear, very desirable from the point of view of secondary combustion.

Secondary combustion itself is a series of purely gas reactions. These reactions are therefore slow compared with those of primary combustion (see p. 200) and adequate time must be provided for their completion. In hand-fired boiler furnaces it was formerly the practice to supply from 4 to 5 cu. ft. of combustion space per sq. ft. of grate area and at the combustion rates formerly used (5 to 10 lb. of coal per sq. ft. of grate area per hr.) this was not inadequate in the case of high-grade coal. When, however, combustion rates were increased with the introduction of mechanical stokers, while the temperature of the combustion gases increased and therefore the rates of secondary combustion also went up, this temperature increase was too slight (see p. 211) to secure

proper secondary combustion in these limited combustion spaces. As a result designers have been increasing combustion space progressively during recent years so that to-day an allowance of 12 to 14 cu. ft. of combustion space per sq. ft. of grate area is not uncommon in new installations which are to be forced to high combustion rates.

Where low-grade fuels are used the fuel bed temperature is low and consequently the temperature of the combustion gases also. This means that the reaction rates of secondary combustion are less and in such cases additional space must be allowed. One of the advantages of Dutch oven construction for these low grade fuels is the provision of increased combustion space coupled with the fact that the products of primary combustion leave the fuel bed at a higher temperature because of absence of radiation from it and therefore burn at a higher rate.

These gaseous reactions can be catalysed by contact with hot refractory surfaces. For this purpose extensive baffles are frequently introduced in the combustion space of boiler furnaces, against which the gases impinge and around which they have to flow. These baffles aid not merely by catalysis of the gas reactions but by improving mixing with the secondary air and by absorption of heat from the gases which in turn is radiated to the boiler. Such baffles are not generally used in chemical furnaces but in many cases their introduction would be highly advantageous. For example, in a muffle furnace a part of the heat from the hot gases is picked up by the wall of the muffle itself but another part is absorbed by the remaining walls of the flue and radiated from there to the muffle. Where the muffle is made of refractory material the temperature difference between it and the remaining walls of the flue is slight because at the high temperature of the furnace the rate of energy interchange between walls and muffle by radiation is very great. If in such a case one will increase the surface area of the remaining walls of the flue, *e.g.*, by allowing alternate bricks to protrude from the wall into the flue, this will furnish additional surface for absorption of heat from the hot gases, which will in turn be radiated to the muffle wall. In this way the capacity of such a muffle can in some cases be increased 100 to 200 per cent.

In many chemical furnaces a baffle of this sort is superfluous. For example, in an externally fired lime kiln the products of

secondary combustion entering the kiln have their combustion catalysed by the surface of the lime itself. As a result combustion in these kilns is unusually perfect.

In order to secure complete combustion one must obviously supply sufficient air, and in practice it is found necessary to furnish a considerable excess. In the limited combustion space of boiler furnaces it is impossible to secure complete oxidation, especially of the CO, even with large amounts of secondary air. Since when carbon burns to CO the heat evolution is less than 30 per cent that of combustion to CO_2, CO going up the stack represents a serious heat loss. Formerly the boiler plant engineer focused attention upon this loss to too great an extent. He determined

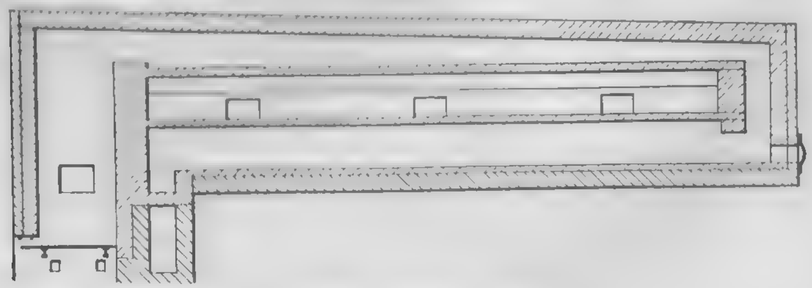


FIG. 49.—Muffle Furnace.

it by analysis of the flue gases and found that excess air cut down the percentage of CO in it. In fact, however, while excess air does reduce the percentage of CO in the flue gas, it reduces the absolute amount formed from the coal little if at all. In other words the CO in the flue gas is reduced by dilution with air rather than by oxidation to CO_2, because the *dilution* cuts down the reaction rate due to the lowering of the temperature of the gases and the time they are in the combustion space almost as much as this rate is increased by a higher concentration of oxygen. Furthermore, in furnaces operated under natural chimney draft it is obvious that the use of excess air increases the volume of flue gas and therefore increases the draft necessary to overcome furnace and stack friction. Since this draft comes only through temperature difference between stack gases and the outside air this means that in such cases stack gas temperature increases with excess air. Consequently excess air runs up stack losses.

On the other hand it is not practicable to reduce excess air too greatly. With grate-fired furnaces it seldom pays to cut it

below 40 to 50 per cent, since otherwise, due to the imperfect mixing and the extremely low reaction rates of secondary combustion caused by the very low oxygen content of the gases at this point, there will be in the flue gases too much carbon monoxide and in some cases even smoke. The better the provision for mixing of secondary air with the products of primary combustion and the greater the combustion space provided, the less excess air required and the smaller the heat losses up the stack. Fortunately in many chemical furnaces (muffles, retorts, pottery kilns, reverberatory furnaces, etc.) the volume of the combustion space and the temperature in it are sufficient to give perfect secondary combustion.

It frequently happens, especially in chemical practice, that it is desired to distribute the heat energy produced by the combustion of fuel at a relatively low but necessarily uniform temperature, over a relatively large area. For this purpose it is impracticable to design a coal-fired furnace so as to provide uniform direct radiation from the fuel bed to all the points to be heated. Experience has shown that the problem can be solved by primary combustion of the fuel upon the grate with the production of a combustible gas, the combustion of which can then be completed after the gas is led to the point where the heat is required. By far the best results are obtained if the gas produced will burn with a smoky flame, *i.e.*, will in its combustion generate a large number of exceedingly fine particles of carbon, which will be heated by the combustion reactions to incandescence and will then transmit the energy of combustion to the desired point by radiation. In practice this can best be secured by the use of a high B.t.u. fuel with a very high percentage of volatile combustible matter, admitting only enough air under the grate to distill off this combustible matter and burn the residual carbon. The volatile matter from such a coal is always rich in carbon, and burns with the smoky flame desired, thus generating a large fraction of the total energy of the combustion of the fuel in the form of radiant energy in the gas flame at a point far removed from the grate on which the fuel is fired.

With a fuel high in volatile combustible matter, producing on coking a large volume of combustible gas, the heat generated in the fire box is to a measure absorbed by the endothermic process of distillation of the fuel itself, and an excessive temperature

in this part of the furnace is avoided. Combustion of this gas is completed in the body of the furnace, thus carrying the heat from the fire box where it is not needed to the back of the charge which would otherwise be too cool.

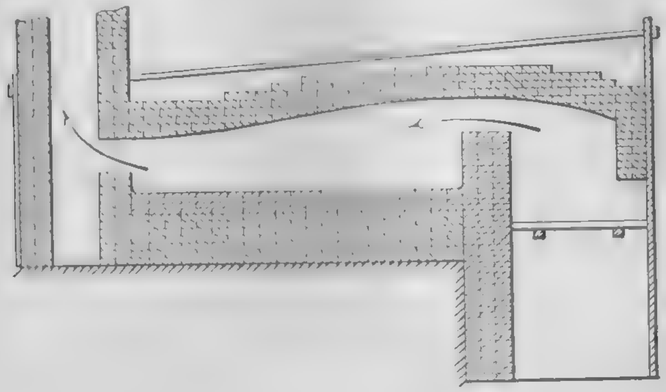


FIG. 50.—Reverberatory Furnace, Short Type.

This type of furnace is employed where it is necessary to bring the whole charge to a uniform high temperature. A large fraction of the heat is transmitted to the charge by radiation from the fuel bed to the arch above the bridge wall from which it is reflected and radiated to the charge. The flue gases going to the stack are obviously hot. It is usually restricted to batch operation.

This is the basis of the utility of the "long flame" of wood which has for many years been the favored fuel for such operations as require a moderate temperature distributed over a large

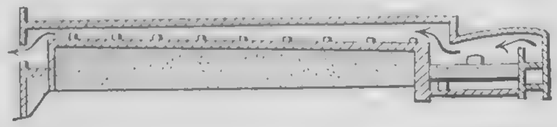


FIG. 50A.—Reverberatory Furnace, Long Type.

This furnace is suitable for preheating the charge when fed through the furnace continuously in a direction counter to the flow of gases. In this particular furnace the stock is worked through by hand stoking and rabbling. Furnaces which provide mechanical conveying of the charge are available. Fuel efficiency is improved by partial recovery of the waste heat from the gases but contact of the gases with the charge is poor and the heat transfer coefficient low in consequence.

area,—such as lime and brick burning. High-grade, high-volatile coals are usually good. The disadvantage of forcing a furnace of large effective area with a low-volatile coal or coke is very great, if a uniform temperature in the combustion space be desired. If the

fire be forced to heat the remote parts of the furnace, the portion next to the fire box is overheated, and this part of the structure rapidly "burns out." If a moderate fire be maintained the output of the apparatus is greatly diminished. This is particularly true, if the charge becomes very corrosive at high temperatures as in making sodium sulphide, or is deteriorated as in burning lime, or if a uniform temperature over a large area is necessary as when a large iron muffle is to be heated as in the Mannheim process for making hydrochloric acid from nitre cake. It is in such cases that an understanding of the principles of combustion discussed in Chap. VI are of great value.

Davis [1] many years ago showed that the output of a coke-fired furnace for making soda by the LeBlanc process was increased by almost 300 per cent by the simple device of introducing an evenly distributed supply of steam under the grate bars. The endothermic reaction

$$C + H_2O = CO + H_2,$$

accomplished three purposes,—first, it reduced the excessive temperature of the fire box and that portion of the furnace hearth adjacent thereto, thus increasing its life; second, it furnished a large volume of combustible gas which passed into the body of the furnace to be burned; third, the presence of that portion of the steam undecomposed diluted the combustible gases and thus lowered the rate of combustion and produced a flame of lower temperature and greater volume. The net result was that the heat supply was evenly distributed over the entire hearth, the output of the furnace increased, and its life lengthened.

The other common endothermic reaction, $CO_2 + C = 2CO$, can also be utilized for producing these results, and from an energy standpoint is even more economical, as it eliminates the heat necessary to produce the steam. Even so low a content of CO_2 as is present in ordinary flue gas is efficient in distributing the heat generated in a fire box over a large area. Not only is the absorption of heat by the formation of CO and its subsequent combustion of value, but the dilution of combustible gases with the accompanying water vapor and nitrogen diffuses the heat by enlarging the volume of flame as already explained. (See p. 219.) When

[1] DAVIS, *"Chemical Engineering."* Davis Bros., Manchester, England (1902).

the flue gas is withdrawn as soon as it leaves the actively heated zone of the furnace, the energy lost by such a procedure is clearly very small compared with the consequent advantages. Eldred

FIG. 51.—Doherty-Eldred Lime Kiln.

The kiln is externally fired. The gases at the top of the kiln are quite cool because of the excellent contact between them and the incoming cold charge. They are piped down to the floor line where the pipe divides, delivering the gas to two blowers, the larger of which discharges most of the gas to the stack while the other recirculates the rest, delivering it below the grate of the two furnaces with which the kiln is equipped. The third blower shown supplies the air. The cut shows only one of the points of entrance of recirculated gas and air, a part of the kiln being cut away to show the interior construction. The discharge pipe for stack gases is also shown cut off.

used this principle in the efficient operation of lime kilns, and it has been frequently employed in heating large muffles, retorts, annealing boxes and containers of this kind. Recently a very valuable application of these principles has been made in the firing of the ordinary red brick kiln. A steam pipe with many small openings is placed throughout the length of each fire box. When the coal fire is well ignited, steam is introduced under the body of the fire. The large volume of low-temperature flame penetrates throughout the entire mass of bricks, giving a larger yield of marketable brick in a much shorter time.

Greater uniformity of heat distribution can be secured by admitting secondary air, not at the bridge wall, but at successive points along the combustion space, the air supply at each point being capable of control. (Semet-Solvay coke ovens, although these are gas-fired.)

It must be remembered that those gases formed by modified primary combustion of low-volatile solid fuel do not burn with a luminous flame, and the process is on that account less satisfactory than the use of a highly volatile coal. In certain cases, however, the combustible gases come into intimate contact with the material to be heated and in such cases the surface of the material itself can serve as a contact mass to catalyse the combustion reactions, provided it is sufficiently hot. Since these reactions take place upon the very surface of the material to be heated, the energy due to combustion is thus generated upon that surface itself and consequently absorbed directly without transmission losses.

If a relatively small area is to be heated to a very high temperature, this dilution of the flame should be avoided, and the fuel and air for combustion must be heated before they combine. It is always possible to preheat the air, but the fuel can be preheated with advantage only when it is a gas. For a localized high temperature even the water vapor present in the air during warm weather has been found to exert a profound influence by the endothermic reaction of its decomposition. Thus in the iron blast furnace at the entrance point of the air blast, an increased melting capacity of the iron reduced is obtained by removing the water vapor from the air used. An atmosphere richer in oxygen than ordinary air is here desirable (p. 241).

2. FURNACES USING LIQUID OR POWDERED SOLID FUELS

Powdered coal was introduced as a fuel over twenty years ago in the burning of cement in rotary kilns. The pulverized coal is injected into the furnace with a powerful blast of air and burns in a flame much the shape of a greatly elongated egg. In large kilns this flame will be from 2 to 4 ft. in diameter at its maximum and 10 to 15 ft. long. Because of the way the fuel is blown in,

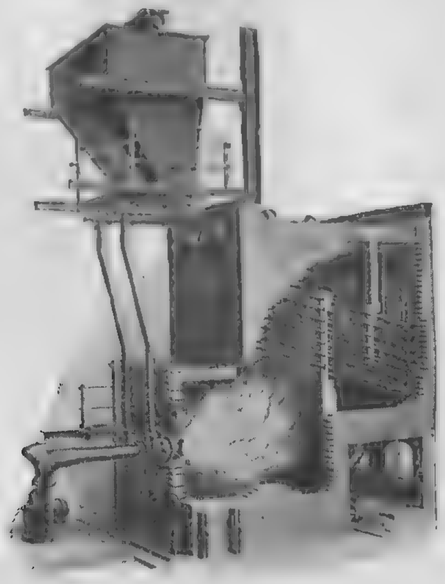


FIG. 52.[1]—Pulverized Coal Fired Boiler.

The semi-dutch-oven construction is provided to furnish ample combustion space. Certain plants are trying the experiment of injecting the coal directly downward through the top of this dutch-oven so that the flame is turned back upon itself. The purpose of this is to give to the ash particles a downward component to sling them into the ash pit. This modification is apparently quite successful.

each particle is surrounded with a layer of air. It is heated to incandescence, partly by conduction but mainly by radiation from the hotter portion of the flame and therefore the volatile matter distills in the presence of excess air. There is therefore little or no tendency to deposit soot provided sufficient air is present for complete combustion of the fuel. The flame from such a burner is exceedingly hot and a large fraction of the heat is given off in the form of radiant energy.

[1] *Courtesy of Fuller-Lehigh Co., Fullerton, Pa.*

One of the disadvantages of powdered coal is the danger of fires and on occasion even of dust explosions. The possibility of the latter can be eliminated by keeping the dust concentration in the air used above the explosive limit. The danger of fires can be reduced by using air-tight ducts for transportation of the powdered fuel and exercising great care to prevent ignition. It is inadvisable to hold large quantities of dust in storage, and grinding equipment should be adequate to supply the maximum demand of the furnace rather than store powdered coal for peak loads. The coal may be transported from the pulverizer to the burner either by screw conveyors or by forcing it along with air pressure (since it flows like a liquid) or by suspending it in air and floating it. In the latter system care must be exercised to keep the air used for floating below the explosive limit.

Liquid fuels are burnt much as powdered coal, being atomized by air under pressure or frequently, on account of its convenience, by steam. They too burn with an extremely hot radiant flame. The simplicity of firing and small combustion space required makes them very advantageous on shipboard.

Both powdered coal and oil can be mixed with air so perfectly that excess air can be reduced to 10 to 20 per cent without danger of incomplete combustion. With both, the short, hot flame tends to overheat that part of the furnace near it, cutting away brick work and injuring a sensitive charge, and coal ash, if fusible, may flux and ultimately disintegrate the furnace lining. The advantages of lowered flame temperature may be secured without sacrificing furnace efficiency by recycling flue gas into the air used for combustion, although this lowers combustion rate, requiring more combustion space; or, dutch-oven construction may be used and the temperature of the combustion products lowered by adding the recycled gas after combustion is complete. Either method is far superior to lowering flame temperature by excess air. In boiler furnaces it is practicable to install water-cooled surfaces at substantially every point in sight of the flame, thereby increasing heat absorption and eliminating fluxing of the walls of the combustion space. Ash dust carried up the stack is sometimes a problem; it has been proposed to remove it by Cottrell precipitation (see p. 332), but the ash is usually so light that the nuisance from it is surprisingly small. The cost of installation and operation of

equipment for powdered coal is high in small units, but this in no wise applies to liquid fuels.

3. FURNACES USING GASEOUS FUELS

In the discussion of coal-fired furnaces it was pointed out that uniformity of heat distribution was best secured by suppressing primary combustion so as to increase the gaseous products and burning these as secondary combustion under controlled conditions. In other words furnace control is best secured with gaseous fuels.

As already stated coal gas and water gas are too expensive for general use while natural gas is available only in restricted areas. In consequence combustion engineers have developed the method of increasing secondary combustion at the expense of primary by isolating the solid fuel furnace and using it for the production of a combustible gas, producer gas (see p. 246). This gas is therefore available for almost any sort of furnace operation.

Since a gas-fired furnace contains little fuel at any one time combustion is under quick and accurate control. Since one can admit the necessary air or gas or both at successive points along the furnace, it is possible to generate the heat exactly where required. Unfortunately none of the cheap gaseous fuels burn with a smoky flame and consequently the heat must be transmitted from the flame to the furnace or charge by conduction rather than by radiation. While this is a disadvantage from the point of view of heat transmission capacity it is a great advantage in maintaining uniformity of temperature throughout the furnace. Even this disadvantage can be eliminated by the use of surface combustion.

Surface Combustion.—The combustion of gases is greatly accelerated by contact with hot surfaces. Furthermore, where the gas burns in this way the heat is generated upon the very surface of the solid and hence raises this solid to incandescence so that while the gas itself is not radiant, the heat evolved by its combustion can none the less be emitted in radiant form. The best way to accomplish this is to mix the gas with air perfectly in as nearly as may be theoretical proportions and burn this mixture by passing it through a porous mass of refractory material such as firebrick or alundum. The contact mass should be porous and

spongy in structure to expose the utmost surface. Where the catalyst is supported horizontally or at not too great an angle it can consist of a pile of small lumps of crushed refractory. Combustion takes place within the mass and the whole becomes highly incandescent. In this way it has been possible to transmit a million B.t.u. per hr. through a single sq. ft. of surface. Despite the short time of contact, combustion is unusually complete and excess air can be reduced to a negligible quantity. To prevent flash-backs the air-gas mixture must be brought through the flues leading to the contact mass at a velocity higher than the rate of flame

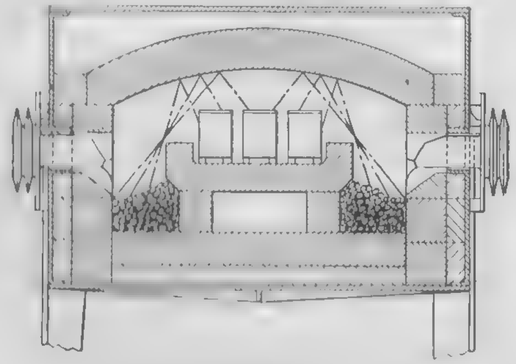


FIG. 53.[1]—Surface Combustion Furnace.

The gas and air mixture enters through the side ports and is directed down upon the coarse mass of refractory material in the bottom of the furnace. From this the heat is radiated up to the arch and down upon the muffle as shown by the broken lines.

propagation through the mixture. In small, cool tubes the allowable velocity is surprisingly low.

While surface combustion in this narrow sense cannot be universally used, surface catalysis plays an important part in every gas-fired furnace. The catalytic action of the walls of the furnace and its flues and of checker work which may be inserted in the combustion space, make it possible to secure complete combustion even at relatively low temperatures. In many furnaces the surface of the charge itself serves this purpose (*e.g.*, pottery, lime and brick kilns, roasting furnaces, etc.).

The pressure drop due to the friction of flow of the gases through gas-fired furnaces can be estimated by the usual equations (pp. 94 to 95). In American practice forced draft is seldom used and consequently gas velocities must be kept low. In simple

[1] *Courtesy of Surface Combustion Co.*

furnaces they are usually between 10 and 15 ft. per second but where the travel is tortuous or the distance is long these figures must be reduced accordingly.

Gaseous fuel is especially well suited for those furnaces in which the temperatures must be controlled exactly at high temperature levels to secure absolute uniformity of heating (open-hearth steel furnaces, pottery kilns, etc.). In such cases unusual attention must be paid to the introduction of the fuel and to the uniformity of its mixing with the air supply and its distribution through the furnace. In ring furnaces and tunnel kilns (p. 230), it is advisable to admit the gas in successive small quantities at a series of points along the furnace. The gas ports must be so located and the furnace so designed as to insure perfect mixing with the air and distribution of the mixture over the charge. The furnace should be so constructed that, if trouble develops, the location of the gas ports and the direction of the gas currents in the furnace can be modified after the furnace has been completed. The ability to control the performance of a furnace in this way is one of the important elements in the skill of a furnace operative.

Three important types of gas-fired furnaces, the ring furnace and the tunnel, and the rotary kilns are discussed on p. 228, under Recovery of Waste Heat.

4. FURNACES USING SOLID FUEL IN DIRECT CONTACT WITH CHARGE

Furnaces of this type include kilns for building bricks, the pig iron blast furnace, the Dietzsch lime kiln (see p. 229), and the ring furnace using solid fuel. The most important illustration of the type is the rotary kiln using powdered coal (see p. 231).

5. ANALYTICAL CONTROL OF FURNACE OPERATIONS

In any given furnace it is usually easy to determine and control the performance of the furnace, *i.e.*, to measure the quantity of the charge, its temperature rise and such chemical changes as may have taken place in it. On the other hand a furnace may be giving satisfactory performance so far as the charge is concerned

and yet be operating very poorly from the point of view of combustion. The heat losses from a furnace are usually restricted to losses in the stack gases, from radiation and in the fuel refuse (ash). Radiation losses are in general not under the control of the operator except as the furnace is redesigned and rebuilt. Lost combustible in the ashes can be determined by proximate analysis (very great care must be exercised in securing a representative sample). However, both these losses are usually small in comparison with those in the stack gases. In consequence the control of furnace combustion depends upon analysis of the stack gases and determination of their temperatures. For example, almost as much information can be secured with regard to the operation of a boiler from determinations of the heating value of the fuel, of the combustible in the ash, and of the temperature and analysis of the stack gases as from a boiler test involving a complete heat balance, at a small fraction of the expenditure of time and labor.

Because of this fact in boiler practice the use of automatic CO_2 recorders is rapidly increasing. Some of these recorders are a mechanically operated Orsat apparatus while others pass the gas sample in series through two orifices, absorbing the CO_2 between the two with solid soda-lime and measuring the CO_2 by the change in pressure drop through the second orifice caused by shrinkage in volume of the gas. In a well-designed boiler furnace the CO will in any case be so completely oxidized by secondary combustion that the CO_2 is a satisfactory measure of the excess air used and the general efficiency of the combustion process. In furnaces so built or operated that this is not the case, CO_2 recorders will not tell the whole story, because one can have the same CO_2 readings with either insufficient or excess air. In the first case there would be considerable CO and perhaps hydrogen in the gas and in the second, excess oxygen. For this reason CO_2 recorders are by themselves of limited value for gas-fired furnaces. Recorders for CO and oxygen have been developed but have not yet earned wide-spread industrial acceptation.

These recorders are valuable adjuncts in furnace control but offer many mechanical difficulties due to dust, delicacy of the working parts, exhaustion of the chemicals and the like. If their indications are to be depended upon they must be carefully and intelligently watched and checked up against an Orsat analysis.

For the purposes of general experimental testing, the Orsat apparatus or some one of its modifications is preferable to the recording instruments.

Errors in Orsat Analysis

As will appear in connection with computations, a small error in the carbon dioxide determination in a flue gas will introduce a serious error in the calculated results. The gas sample in an Orsat is ordinarily collected over water. This water dissolves some of the CO_2 and in consequence makes the CO_2 determination in the gas low.[1] Mercury should always be employed in the burette in gas analyses where precision is desired. The extent of the error can be judged from the following data taken from Bulletin 2 of the U. S. Bureau of Mines.

In boiler test No. 2, reported by the Bureau in this bulletin, the dry coal has an ultimate analysis of 60.15 per cent C, 4.35 per cent H, 21.18 per cent O, 1.07 per cent N, 0.72 per cent S and 12.53 per cent ash. The mols of H_2 per 100 lbs. of coal are therefore 4.35/2.016 and the atoms of oxygen, 21.18/16. The difference is 0.833, the mols of net hydrogen (H_2). The ratio of carbon to net hydrogen (C/H_2) is therefore $60.15/(12)\ (0.833) = 6.03$. Correcting for sulphur, the ratio is 5.57, the lowest value which can possibly be ascribed to it from the ultimate analysis. Since the ash from the furnace was 8.61 per cent of the dry fuel fired and contained 15.1 per cent carbon, 2.16 per cent of the carbon in the fuel remained unburnt in the ash. Hence, the ratio of C/net H_2 in the flue gas should be 5.89, or corrected for sulphur, 5.45.

[1] Assume for example a gas consisting of 11 cc. of CO_2 and 90 cc. of other non-acidic gases. When 101 cc. are introduced into the Orsat, 1 cc. of this CO_2 may well dissolve, leaving what is apparently 100 cc. sample. There will therefore be a shrinkage of 10 cc. over caustic. When the sample is returned from the caustic to the burette the volume will gradually increase owing to the escape of the CO_2 from the water into the gas due to its lowered partial pressure, but on the second or third treatment of the gas with caustic the volume will again return to 90 cc. This is one cause of the apparently slow absorption of CO_2 in caustic in gas analyses. It will be noted that the analysis is apparently 10 per cent CO_2 whereas actually there were nearly 11 per cent in the sample.

The flue gas analysis is given in the table below:

		C	O_2
CO_2	10.04	10.04	10.04
O_2	9.04	.....	9.04
CO	0.10	0.10	0.05
N_2	80.82	.....	.....
		10.14	19.13
	O_2 from air $= 80.82\ (20.9)/79.1 =$		21.355
	O_2 = net H_2 in fuel =		2.225
	Net H_2 =		4.45
whence			
	C/net $H_2 = 10.14/4.45 =$		2.28

It is seen that the gas analysis gives a ratio of carbon to net hydrogen less than half the real value. The unburnt combustible in the ash gives an error of this sign but to explain its magnitude by such an assumption would mean that 60 per cent of the carbon in the coal remained unburnt in the ash. The error actually arises from the fact that the CO_2 determination in the flue gas is low by about 1 per cent. If one assumes the CO_2 value higher by that amount the analyses check. Mercury in the burette would have avoided this error.

Note that since the amount of the flue gases is figured from a carbon balance this introduces an error of 10 per cent in calculating them and hence a similar error in getting the stack losses in a heat balance. The latter is no unimportant matter.

A point, failure to appreciate which sometimes offers difficulty, is the fact that a gas analysis, even when made over water, is none the less an analysis on the dry basis. Since at room temperature the gas measured in a burette above water is over 3 per cent water vapor this fact is not obvious. It must, however, be remembered that all measurements are made at the same temperature and therefore with the same partial pressure of water vapor in the gas, so that if half the gas is absorbed by some reagent, half the water vapor in the gas as originally measured condenses out. It is as though the analysis were carried out, not at atmospheric pressure, but at a constant pressure equal to atmospheric less the vapor pressure of water at the temperature of the analysis. Where the analysis is carried out with mercury it is necessary to have a drop

of water present to keep the gas saturated or else to dry the gas completely before measuring, since otherwise the partial pressure of water vapor in the gas would vary with that over the absorbents employed.

6. RECOVERY OF WASTE HEAT FROM FURNACES

In every furnace reaction it is required either (*a*) to heat the charge up to some specified temperature (calcining reactions, and the like), or (*b*) to furnish at such a specified high temperature the heat necessary to carry out some reaction (*e.g.*, decomposition of limestone, fusions, etc.). In either case a definite amount of heat is required at or above a definite temperature. When a fuel is burned, the maximum temperature attainable is limited by either (1) the temperature at which the reversal of the combustion reactions becomes serious, or (2) by that temperature to which the heat set free by the combustion will raise the products of combustion. By the use of a given fuel it is impossible to exceed the temperature limit fixed by the first of these conditions but it is possible to avoid the second.

Furthermore, since the oxygen essential for combustion, coming as it does from the air, brings with it nearly four times its volume of inert nitrogen with its large heat absorption capacity, it is not surprising that very frequently the second of these limiting conditions is the important one. In illustration assume a producer gas whose heat of combustion will raise its own combustion products to only 1500° C. If now it be required to use this gas to carry out a reaction at 1400°, it is evident that but a small fraction of its heating value will be usefully available, as most of it will be wasted as sensible heat in the flue gases. If, however, this waste sensible heat be utilized to preheat the charge, fuel, and air to a temperature at least approximately that of the reaction, 1400°, most of this heat may be usefully recovered, and the fuel consumption of the process reduced to a small fraction of that otherwise necessary.

Counterflow

To accomplish this effectively it is evident that the principle of counter current flow of the materials between which this interchange of sensible heat is desired must be employed, *i.e.*, that the heat content of the waste products, while still very hot, must be used only to attain the final increment in temperature in the incoming materials, while the preliminary heating of these materials must be accomplished by heat flow from the reaction products after the latter have been considerably cooled.

The utilization of this principle of waste heat recovery is essential in the efficient operation of all high temperature furnaces. Even in the most common low-temperature furnace—the steam boiler—it is successfully employed in the "economizer" used to preheat the feed water with the waste heat in the stack gases. The simplest means of realizing these conditions is to allow the gaseous combustion products to flow over and through the incoming solid or liquid charge in direction opposite or counter to the motion of the charge, while the air essential for combustion enters in contact with the hot solid or liquid products of the furnace reaction, here again the motion of the two being counter to each other.

Dietzsch Kiln

Such methods of heat regeneration particularly applicable to direct-fired furnaces which, though effective and much used abroad, have been little employed in the United States, are illustrated by the Dietzsch kiln and the Hoffman ring furnace. The simple shaft furnace in which charge and fuel are fed at the top does not permit of effectively preheating the charge and cooling the waste gases, because combustion would start near the top and leave no space for preheating.

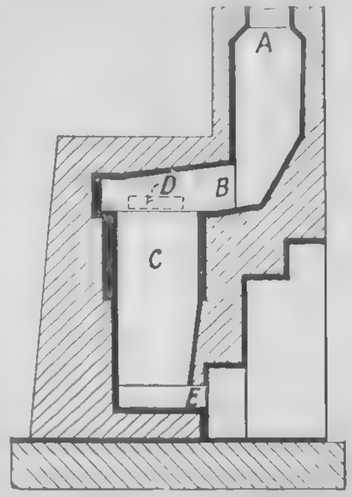


Fig. 54.—Dietzsch Kiln.

The Dietzsch kiln is a shaft furnace so designed that the fuel is admitted half-way down the shaft, and thus premature combustion is avoided.

It consists of a vertical shaft furnace having a horizontal middle portion or shelf as shown in Fig. 54. The charge is introduced at *A*, and descends through the shaft to the platform *B*. Here it

is mixed with fuel introduced through *D* and drops into the shaft *C*. Air is drawn in through *E*. Active combustion takes place at the top of *C*, the hot flue gases preheating the charge in *A*, while the hot reaction mass descending through *C* to the discharge *E* preheats the incoming air. Tests run on such furnaces show a very high fuel economy but operating labor costs are excessive.

Hoffman Ring Furnace

The Hoffman ring furnace is extremely efficient, and has added advantages in all industries which demand a period of gradual heating up and slow cooling. It is gratifying to note the increasing applications of this arrangement in American industries. As originally developed for solid fuel it consists of a circular, elliptical, or rectangular gallery, built around a central flue. This gallery (Fig. 55) is divided into separate chambers, each constructed with side openings, *E*, a door on the outside, *C*, and a flue *D* to the central stack, *A*, and so provided with diaphragms and dampers that any passage may be closed at will.

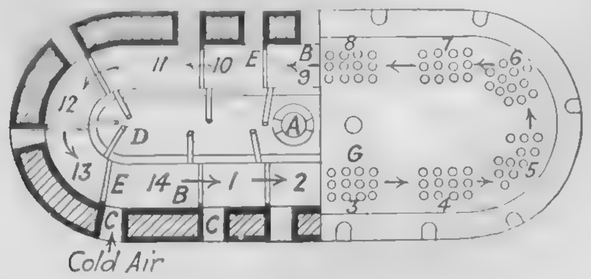


Fig. 55.—Hoffman Ring Furnace for Solid Fuel.

In operation, combustion is carried on in only one chamber at a time. The two chambers opposite this are in the process of charging and discharging, and all the others are either being heated up to the combustion temperature by flue gases or are themselves cooling and thereby preheating air for combustion. Air enters through the door of the discharging chamber (No. 1 in a series of 14 in the furnace shown) and is drawn through the adjacent chambers in series (2, 3, 4, 5, 6) until it reaches the active one (7); these chambers contain burned product which preheats the air and is itself cooled. From the active chamber the hot flue gases pass through chambers 8, 9, 10, 11, 12 and 13, heating up the unburned charge there, and finally pass to the stack through the flue *D* in chamber 13. No. 14 is meanwhile being recharged and is totally shut off from the rest. After ignition in the active chamber is completed the adjacent one which has not been burned (8) is then made active by admitting fuel to it through holes in the top; the newly charged chamber (14) is admitted to the series by connecting it to the stack and to 13 and closing the flue from 13 to the stack, the discharged chamber (1) is charged, and the coolest burned chamber (2) is opened to the air and discharged.

It is obvious that very efficient counter-current action is obtained in this furnace and therefore the heat consumption is exceedingly low. Pre-ignition is avoided by not admitting the fuel until the chamber is ready to be burned. The chief disadvantages encountered are high initial expense and labor costs, and the mechanical stresses set up by repeated heating and cooling.

The Hoffman ring furnace is operated most smoothly and efficiently with gaseous fuel, and all modern construction, at least in this country, is of this type. The gas may be admitted to a number of chambers simultaneously, thus avoiding localized overheating. Because of the very efficient preheating of the air used for combustion, high temperatures can be successfully realized even with a fuel of low heating value (producer gas), and the large volume of gas flowing through the chambers gives uniformity of heat distribution. A gas-fired furnace is shown in Fig. 55*A*.

These furnaces must be built carefully, to provide for the repeated expansion and contraction in each chamber. Especially where high temperatures are to be employed, only the highest grade refractories can be used in construction.

Rotary Kiln

By the use of powdered coal in a blast of air it has become possible to introduce solid fuel into a furnace with perfect regularity, and by providing a means of passing the flame produced through the charge efficient heating is realized. This can be done in a rotary kiln, consisting of a boiler-plate, tubular shell from 30 to 220 ft. long, 6 to 12 ft. in diameter, and lined with fire brick

or other resistant material, the choice of refractory depending upon the reaction to be carried on. The charge is heated by introducing centrally into the kiln a stream of powdered coal injected

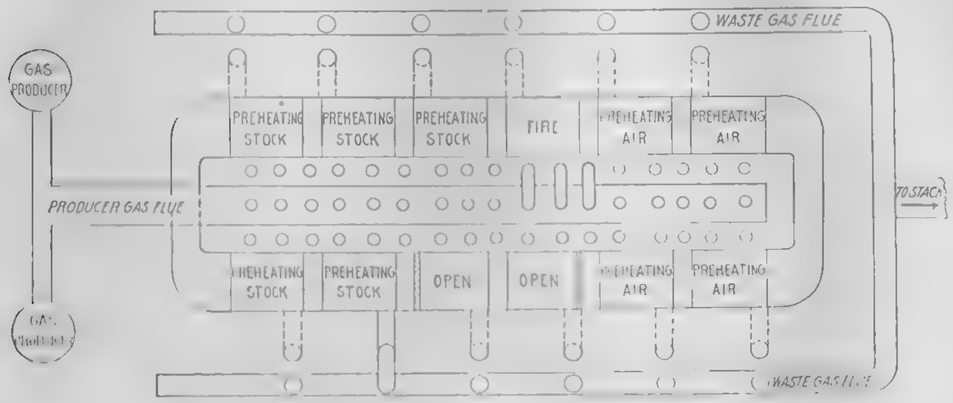
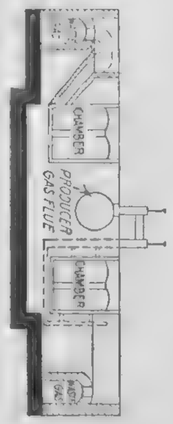


FIG. 55A. Hoffman Ring Furnace for Gaseous Fuel.

The fuel is distributed through a central flue from which connection is made to the chambers under fire by means of a number of inverted U-tubes, each of which is inserted into a hole in the main flue and into the top of one of the distributing flues around the chambers. The control valves are located in the U-tubes. From each of the latter flues a large number of distributing ports lead to the chamber in order to provide uniformity of gas distribution. Furthermore a number of these distributing flues are fed simultaneously, only a small amount of gas going to each, to avoid localized overheating. From the proper chamber connection is made to the stack by a method similar to that used in distributing the fuel. The holes into which the distributing U-tubes fit are covered when not in use.

All flues must be liberal in size in order to avoid excessive friction with the large amount of air and gases to be handled. In order to insure uniformity of heating and cooling especial care must be exercised in packing the charge and in the construction of the ports in the separating walls between chambers as well as in the distribution of the producer gas delivered to the chambers under fire.



with air, and by slowly rotating the furnace, thus causing the contents to constantly follow the shell toward the top and drop or roll through the flame. Furthermore, if the furnace be inclined at a moderate angle from the horizontal, the material is regularly moved forward until discharged. Such a furnace may be operated either parallel or counter current, and charged either intermittently or continuously. Operated counter current it obviously

gives some heat recovery but far inferior to that of the ring furnace because of poorer contact between charge and gases. Its great advantage is low operating and labor expense and it consequently is of unusual importance in this country where fuel is cheap and labor high.

As discussed on p. 211, the most rapid transfer of energy takes place when it is in the form of radiant heat. Powdered coal furnishes an ideal source of this form of energy and this type of furnace seems to be capable of much larger utility than it at present enjoys. If the charge is a liquid or a liquid suspension it may be atomized by a spray nozzle into the combustion space and both evaporation and combustion, calcination or other chemical reaction carried on with great rapidity; if a fine powder, it may be agglomerated into small pellets or lumps, by tumbling it with a small amount of suitable binder such as tar or sodium silicate solution. The mechanical devices for supporting the shell and for taking up the downward thrust due to rotation, and the driving mechanism have all been thoroughly developed and are easily obtained on the market.

One disadvantage incident to the ordinary type of rotary kiln is the difficulty with which an efficient heat regeneration system for preheating the air can be employed in connection with it. Such difficulties are, however, by no means insurmountable, and it is but a question of time when the economy in fuel will compensate for the expense of such an installation.

If the clinker and ash from the solid fuel used in these furnaces is objectionable from the point of view of the product, it is obvious that they must be fired by gaseous fuels. Solid fuels may, however, be used by providing a fire box and grate apart from the reaction chamber, and leading the flame over a bridge wall to the charge.

Tunnel Kiln

Another type of furnace which, like the above, gives countercurrent flow of charge on the one hand, and air and flue gas on the other, and hence offers excellent heat regeneration in the furnace itself, is the *tunnel kiln*. It has been developed in recent years for firing materials that cannot be tumbled, as in a rotary kiln,

and yet which require a shorter time of heating and cooling than the cycle of a ring furnace. It consists of a tunnel, through which are pushed a number of trucks carrying the charge. The trucks run on a steel track and running gear, but the whole superstructure on the truck may be of refractory material, and the lower part protected from the heat by the shape of the tunnel, or in some cases by the use of a seal consisting of a trough filled with sand, into which dips an apron attached to the body of the truck. These kilns are usually gas fired, the fuel being admitted near the

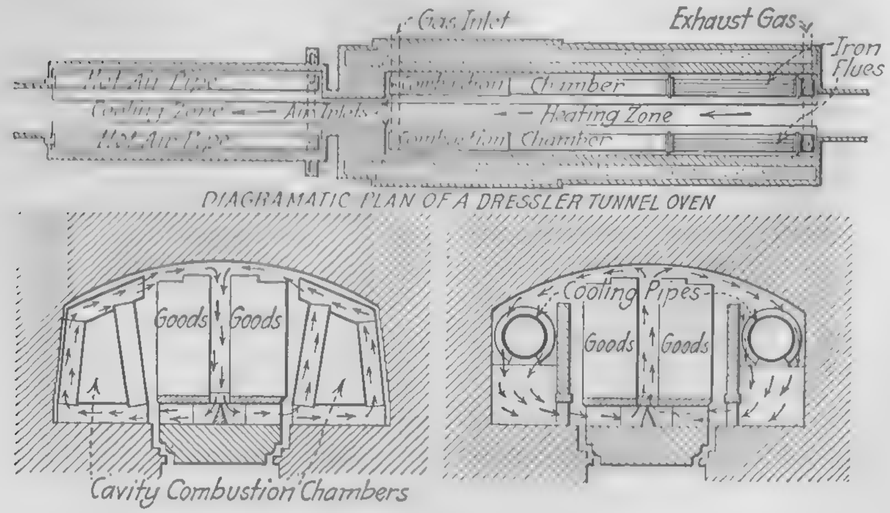


FIG. 56.—American Dressler Tunnel Kiln.

The streams of arrows indicate the "thermo-syphon" circulation of the gases. This reverses direction in the heating and cooling zones.

middle of the tunnel. They offer excellent control of the heating operation, and are successfully used up to 1400° C. They represent an extremely important phase of modern furnace development.

In cases in which the charge is small in amount, or in which it is inadmissable to bring charge and combustion products into contact because of chemical interaction (as is usually true in the use of muffles and retorts), the sensible heat of the gaseous products of combustion must be employed to preheat the fuel and air. Actual contact is here out of the question, but two means are available to effect the heat recovery. In the first fuel and air may enter separately (to avoid premature combustion) through

suitable channels in a preheater, separated from the combustion products by partition walls through which the interchanged heat flows, the motion of the combustion products leaving the furnace being opposite or counter to that of incoming fuel and air. Such is known as the "recuperative" system of heat recovery or preheating. Its value is seriously limited by the fact that for high-temperature furnaces no cheap metal is available for the partition walls which will withstand the corrosive action of the hot gases, while the refractory earthenware ducts which must in consequence be employed are expensive, fragile, porous, and poor conductors of heat. This system is therefore not widely used but affords a uniformity of preheating obtainable in no other way.

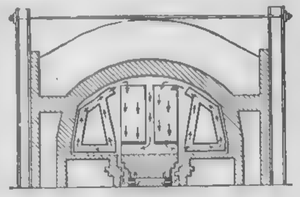


FIG. 56A.—Sectional Elevation of Dressler Tunnel Kiln, Showing Circulation of Gases through the Stock.

The other means available for heat recovery in such cases consists in allowing the combustion products to escape through and heat up chambers filled with refractory material in the form of "checker-work," as large in amount and with as large a surface as possible, while the incoming air and fuel (if gaseous) are preheated by passage through similar chambers previously heated in this same way.

It is necessary to provide only two channels for the fuel gas and two for the air. While one channel of each pair is being heated by the flue gas leaving the furnace, the other two are being cooled by the incoming fuel gas and air. Or, to state it in another way, while the flue gas is giving up its valuable heat to the bricks of two of the chambers, the bricks of the other two are returning the heat to the gas and air to be carried back into the furnace. This is the "regenerative" system of heat recovery, but a more accurate term would be a "reusing" system. By periodically changing the channels from hot flue gas to cold air and fuel gas by the use of "butterfly" valves, a great amount of heat otherwise lost is retained in the furnace cycle. It has the advantage in construction simplicity, but requires constant attention in operation and gives temperature fluctuations caused by the temperature variations of the chambers during each cycle. It would at first appear that this system does not offer the advantages of counter-current operation, but if air and fuel gas flow

through the chambers in a direction opposite to that of the combustion products, effective counter-current action is realized. The hot flue gases entering the first end of the chamber bring this end up to a high temperature, but the other end attains only a moderate heat since the flue gases have already cooled to a great degree; upon reversal, the cold air flowing in the opposite direction is first warmed by contact with this other relatively cool end of the chamber, but is finally raised to the highest possible temperature by contact with the hottest bricks in the first end.

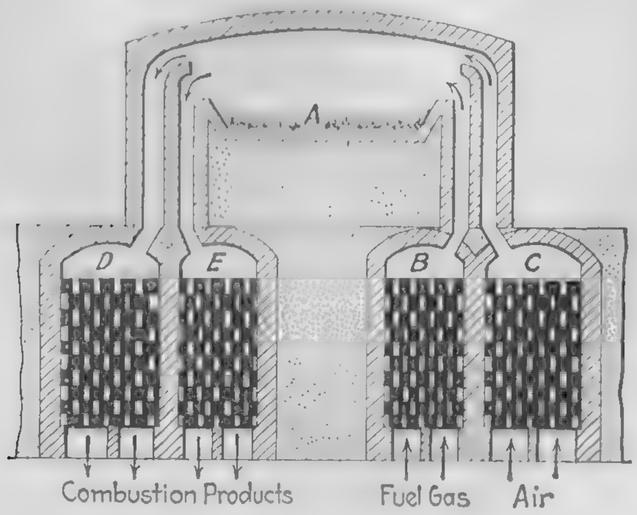


FIG. 57.—Open-Hearth Furnace with Regenerative Checkers.

Reversing valves and connecting flues are not shown. Attention should be called to the fact that the air chambers are larger than those for gas because of the larger volumes to be handled. The construction of the furnace itself is of extreme importance in order to secure uniform distribution of the flame throughout the furnace.

In one special case, that of the iron blast furnace, while it is absolutely necessary to preheat the air needed for combustion in order to produce the large quantity of heat required at the high temperature essential for the fusion of the iron, nearly all the sensible heat of the furnace gases is used up in preheating the charge of ore, flux, and fuel in the upper part of the shaft of the furnace itself, and little is left to preheat the air. In this case a series of chambers or "stoves" of the regenerative type is used, these being heated by burning in them a part of the waste fuel gas from the top of the blast furnace itself. These stoves are tall,

cylindrical steel shells, lined with firebrick, and filled with firebrick checkerwork or flues.

Regenerative furnaces must be carefully built of highly resistant brick, so placed as to secure good contact of brick surface with the gas, yet in such a way as not to introduce too great resistance to flow, and so designed as to resist the expansion and contraction with temperature changes to which they are subjected. Fortunately, as pointed out above, the temperature changes at *any one spot* are not excessive. They are placed sometimes beneath, sometimes beside the furnace, and are usually rectangular. High heat conductivity, produced by high gas velocity, can be secured, though at the expense of increased frictional resistance, by having them long and narrow, but exigencies of construction often make this impracticable.

The effectiveness of regenerative checkers in recovering heat depends directly upon the coefficient of heat transfer between the checkers or flues and the gases which pass through them. During the heating up of the checkers they are at a temperature lower than the hot flue gases passing through them to the stack. The heat picked up from these gases and consequently the temperature to which they fall before reaching the stack is controlled by the existing temperature difference between the checkers and gas and by the coefficient of heat transfer. Similarly the average temperature to which the checkers fall during the air blow depends upon the heat transfer during this part of the cycle. The periodic reversal of direction of heat transfer makes calculation somewhat complicated.

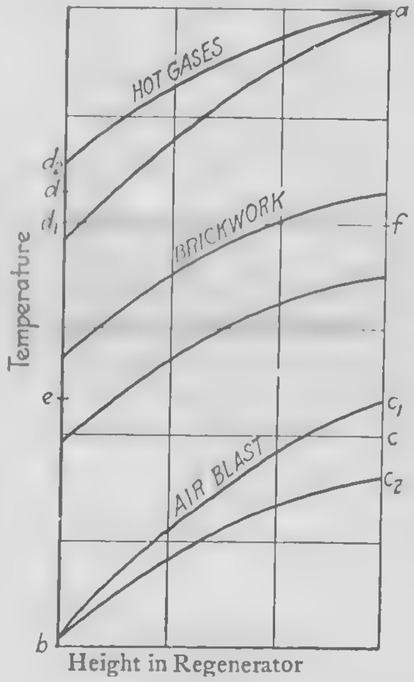


FIG. 58.

The curves in Fig. 58 indicate diagrammatically the temperature conditions in a regenerator in which it is assumed that the air

enters at the bottom and leaves at the top while the flue gases flow downward in the opposite direction. The upper of each of the three sets of curves indicates the temperature conditions at each particular point in the regenerator at the end of the heating cycle just prior to reversal of the valves or at the beginning of the air blow. The lower curve of each pair indicates the corresponding conditions at the end of the air blow or just after the flue gases are turned through the checkerwork. At the start of the air blow the brickwork is hot and the air temperature curve is therefore high. As the air blow progresses the brickwork cools off and the air temperature curve falls correspondingly. The average temperature reached by the air is indicated by point c. After reversal the flue gases entering the cool checker are lowered in temperature as indicated by the lower of the curves, ad_1. However, as the brickwork rises in temperature the heat recovered from the flue gas is lessened and temperatures finally rise to a point indicated by the upper of the two curves, ad_2. The average temperature of the gases going to the stack is d.

The average difference in temperature between the brickwork and air during the air blow, and between the hot gases and the brickwork after reversal, does not change greatly from top to bottom of the regenerator. It is therefore allowable to use an arithmetic mean temperature difference for the average temperature differences in the system. In other words it is allowable to write:

Average temperature difference between gas and brick,

$$(\Delta t)_G = \frac{(a-f)+(d-e)}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Average temperature difference between brick and air,

$$(\Delta t)_A = \frac{(f-c)+(e-b)}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Within the velocity ranges encountered it is allowable to assume the coefficient of heat transfer proportional to the velocity:

$$h_G = \alpha N_G/Am;\ h_A = \alpha N_A/AM. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The total heat quantity transferred per minute from hot flue gas to the brickwork is

$$\frac{N_G(a-d)s}{m} = \frac{\alpha N_G B}{Am}\left[\frac{a-f+d-e}{2}\right], \quad . \quad . \quad . \quad . \quad (4)$$

and similarly from brick to air,

$$\frac{N_A(c-b)S}{M} = \frac{\alpha N_A B}{AM}\left[\frac{f-c+c-b}{2}\right]. \quad . \quad . \quad . \quad . \quad (5)$$

Adding Eqs. 4 and 5, one obtains:

$$(a-d)s+(c-b)S = \frac{\alpha B}{A}\left[\frac{a-c+d-b}{2}\right]. \quad . \quad . \quad . \quad . \quad (6)$$

The heat balance per cycle is as follows:

$$N_g\,(a-d)s - R_g = N_a\,(c-b)S + R_a = pw\Delta \quad . \quad . \quad (6a)$$

where R_g and R_a represent the heat lost per cycle, by radiation and conduction to the surroundings, on the gas and air blows, respectively.

Nomenclature

(All quantities are averages per cycle.)

a = temperature of entering hot blast °F.
b = temperature of entering air °F.
c = temperature of leaving air °F.
d = temperature of leaving hot blast °F.
e = temperature of brick at cold end °F.
f = temperature of brick at hot end °F.
N_G = mols of hot gas per cycle.
N_A = mols of air per cycle.
p = sp. ht. of checkerwork.
m = minutes on gas side.
M = minutes on air side.
s = molal heat capacity of gas.
S = molal heat capacity of air.
A = av. free cross-sectional area in sq. ft.
B = total heating surface exposed in sq. ft.
h_G = coefficient of heat transfer between hot gas and brick.
h_A = coefficient of heat transfer between brick and cold air.
W = lbs. brickwork in the regenerator.
Δ = average fluctuation in temperature of checkerwork.

In any problem in design the quantities a, b, and the ratio of N_A/N_G are given by the very conditions of the furnace operation for which the regenerative system is to be constructed. In general too, either c or d is fixed, the former by the amount of preheating it is desired to secure in the air or the latter by the allowable temperature to which the flue gases may be dropped without interfering with stack draft. Whichever of these two quantities is known the other may be calculated immediately by the heat

balance of Eq. (6*a*), which involves radiation losses. By combination of Eqs. (4) and (5) one secures the following expression for $f+e$ which appears in both of them:

$$f+e=\frac{S(a+d)\ (c-b)+s\ (a-d)\ (c-b)}{s(a-b)+S(c-b)} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The allowable rise and fall in temperature of the brickwork from its maximum to its minimum points is determined by the allowable fluctuation in the temperature of the preheated air or of the flue gases going to the stack. The brickwork temperature will vary about half as much as these gas temperatures. Inserting this allowable fluctuation in brickwork temperature (Δ) into Eq. 6*a*, one obtains the ratio of the amount of brickwork in the regenerator to the amount of gas per cycle, W/N_a. Theoretically one can give to W and N_a any values desired. If both be small the regenerator must frequently be reversed. The larger the regenerator (*i.e.*, W) the less frequently is this necessary. Once W is chosen, N_a is fixed from (6*a*). The ratio of B/A is determined by Eq. (6), which calls for the coefficient α.

The majority of blast furnace stoves uses flues rather than checkers. From a relatively large number of tests of such equipment[1] the value of α is found to average 0.07 when the stoves are clean and to fall to 0.04 or even lower when the stoves are dirty. If one calculates from these values the ordinary coefficients of heat transfer one finds them approximately twice those given by the Dixon equation (p. 149). This is probably due to the marked roughness of the flues. Checkerwork regenerators in which the gases flow in a staggered path around the bricks give values of approximately 0.6. The coefficients for checkerwork are somewhat more than double those given by the equation for staggered flow (p. 152), and the reason is probably the same.

The pressure drops through such checkerwork or flues can be estimated in the usual way (p. 93). In this country the velocities employed are very low (5 to 10 linear ft. per second) because dependence is usually had upon stack draft. As the cost of fuel goes up the necessity for heat recovery will increase, regenerators

[1] JOHNSON, "Blast Furnace Construction," McGraw-Hill Book Company, Inc., 1917, p. 230. DIEHL, *Eng. Soc. W. Pa.*, Dec., 1912. LITINSKY, *Feuerungstechnik*, 1917, V, p. 149. MACCOUN, *Yearbook Am. Iron and Steel Ind.*, 1915.

will be built larger or else be operated at higher gas velocities, and the necessary pressure drop will be overcome by forced draft.

Air consists of 79.1 per cent by volume of nitrogen. Since the specific heat is nearly the same as that of oxygen, it may be seen that a great saving in heat could be effected if the oxygen content of the air used could be increased. For some purposes this will be accomplished with much profit in the near future. This possibility of saving is, however, a practical rather than a theoretical one, as it should be possible by the methods of recovery just described to preheat all the nitrogen entering the furnace with the sensible heat of that leaving it, but the present preheaters required are large, expensive and relatively inefficient.

7. CALCULATIONS[1]

The general methods of thermal calculation of furnace problems will be illustrated by the following computations on a gas-fired continuous preheating furnace.

TEST DATA

Duration of test	12 hours
Stock fed, total	542,020 lbs.
Av. temp. of stock fed	86° F.
Ave. temp. of stock discharged	1167° C.
Ave. sp. ht. of stock	0.153
Fuel gas consumption, saturated with water vapor at 86° F. and 29.5 in. bar	1,301,000 cu. ft.
B.t.u. per cu. ft. of gas (water condensed) at 86° F. and 29.9 in. bar	517
Ave. fuel gas temp. (100 per cent rel. hum.)	86° F.
Ave. air temp.	86° F.
Ave. air rel. hum	53 per cent
Ave. gas temp. entering stack	843° F.

Average gas analyses:

	Leaving Furnace	Entering Stack
CO_2	8.24	4.51
O_2	1.15	12.05
CO	5.34	0.12
N_2	85.27	83.32
Total (dry basis)	100.00	100.00

[1] See also under Gas Producers, pp. 257 to 259.

Fuel Gas (Dry Basis):	Per cent
CO_2	2.3
Illuminants	3.3
O_2	0.4
CO	7.0
H_2	53.0
CH_4	29.0
N_2	5.0

Preliminary Calculations.

(1) *Basis*: 100 *mols of dry fuel gas*:

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	2.3	2.3	.....	2.3
Ill.*	3.3	9.9	9.9	.....
O_2	0.4	.....	.....	0.4
CO	7.0	7.0	.....	3.5
H_2	53.0	.....	53.0	.....
CH_4	29.0	29.0	58.0	.....
N_2	5.0	.....	.....	.....
Totals	100.0	48.2	120.9	6.2

* Taken as equivalent to C_3H_6.

(2) *Basis*: 100 *mols dry flue gas at furnace.*

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	8.24	8.24	.....	8.24
O_2	1.15	.....	.....	1.15
CO	5.31	5.31	.....	2.67
N_2	85.27	.....	.....	.....
Totals	100.00	13.58	.....	12.06

(3) *Basis*: 100 *mols dry flue gas at stack.*

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	4.51	4.51	.....	4.51
O_2	12.05	.....	.....	12.05
CO	0.12	0.12	.....	0.06
N_2	83.32	.....	.....	.....
Totals	100.00	4.63	.....	16.62

Ratio of air to fuel gas—Basis: 100 *mols dry fuel gas.*

(1) *At furnace.*

By *carbon* balance.

$48.2 = 0.1358y$; whence $y = 355$ mols dry flue gas.

By *nitrogen* balance.

$0.791x + 5.0 = 0.8527\ (355)$; whence $x = 377$ mols dry air,

$\frac{377}{100} = 3.77$ mols dry air per mol of dry fuel gas.

(2) *At stack.*

$48.2 = 0.0463y$; $y = 1040$ mols dry flue gas,

$0.791x + 5.0 = 0.8332\ (1040)$; $y = 1088$ mols dry air,

$\frac{1088}{100} = 10.88$ mols dry air per mol of dry fuel gas.

(3) *Flue leakage.*—The increase in air from furnace to stack is obviously leakage. Since the basis is fuel gas, air quantities may be subtracted directly, *i.e.*, the in-leak of dry air is $10.88 - 3.77 = 7.11$ cu. ft./cu. ft. of dry fuel gas.

Mols O_2 theoretically required for fuel $= 48.2$ (for carbon) $+ \frac{120.9}{2}$ (for H_2) $= 108.65$. Since the fuel contains 6.2, the difference, 102.45 mols O_2, requires $\frac{102.45}{0.209} = 491$ mols of dry air.

Mols dry air in flue gas per mol of dry air theoretically required.

(*a*) *Leaving Furnace.*

$\frac{377}{491} = 0.768$; excess air $= -23.2$ per cent.

(*b*) *Entering Stack.*

$\frac{1088}{491} = 2.22$; excess air $= +122$ per cent.

Overall Heat Balance; Basis $= 12$ *hrs.*

$$1{,}301{,}000\ \frac{(29.5 - 1.248)}{(29.9 - 1.248)} = 1{,}285{,}000$$ cu. ft. sat. fuel gas at 86° F. and 1 atm., since pressure of water vapor at 86° F. $= 1.248''$.

Input (in Fuel Gas).

$(1{,}285{,}000)\ (517) = 664{,}000{,}000$ B.t.u.

$$1{,}285{,}000\ \frac{(492)}{(546)\ (359)} = 3220$$ mols sat. fuel gas.

$$3220\ \frac{1.248}{29.5} = 136.5$$ mols *moisture* in fuel.

$3220 - 136 = 3084$ mols dry fuel.

$(100)\ (136.5)/3084 = 4.42$ mols moisture per 100 mols dry fuel.

Mols water from *burning* 100 mols dry fuel = 120.9.
Total from 100 dry fuel = 120.9 + 4.42 + 125.3.
Partial pressure of water in air = (0.53) (1.248) = 0.662 in. mercury.
Partial pressure of air = 29.5 − 0.66 = 28.84 in. mercury.

$$\text{Moisture from air} = \frac{(1088)\ (0.662)}{28.84} = 24.9 \text{ mols.}$$

Mols Moisture in Stack gas.

From fuel	= 125.3
From air	= 24.9
Total	150.2

Latent Heat up Stack—12-*hr. Basis.*

$$\frac{3084}{100}\ (150.2)\ (18)\ (1043) = 87{,}100{,}000 \text{ B.t.u.}$$

Potential Heat up Stack—12-*hr. Basis.*

$$\frac{(3084)\ (1040)\ (0.0012)\ (68{,}000)^*\ (1.8)}{100} = 4{,}710{,}000 \text{ B.t.u.}$$

* 68,000 gm. cal. evolved by burning 1 gm. mol. of CO to CO_2.

SENSIBLE HEAT UP STACK ABOVE 86° F., PER 100 MOLS DRY STACK GAS
SENSIBLE HEAT, B.T.U. PER MOL

Gas	Pound Mols	At 843° F.	At 86° F.	Difference	B.t.u. Loss
CO_2	4.51	8,200	536	7,664	34,600
CO, O_2, N_2	95.49	5,680	384	5,296	505,000
H_2O vapor	14.44*	6,800	492	6,308	91,100
Total					630,700

* (150.2/10.4) = 14.44 mols total H_2O vapor per 100 mols stack gas

Total Sensible Heat up Stack above 86° *F.*—12-*hr. Basis.*

$$(3084)\ (10.4)\ \frac{630{,}700}{100} = 202{,}400{,}000 \text{ B.t.u.}$$

Heat into Charge—12-*hr. Basis.*

$$(542{,}020)\ (0.153)\ (2135 - 86) = 170{,}000{,}000 \text{ B.t.u.}$$

DISTRIBUTION OF HEAT

	B.t.u./12 hrs.	Per cent of Input	
Input (in fuel)	664,000,000	100.0	
Output:			
Into charge	170,000,000		25.6
Stack losses:			
(*a*) Potential	4,710,000	0.7	
(*b*) Latent	87,710,000	13.1	44.3
(*c*) Sensible	202,400,000	30.5	
Unaccounted (radiation, cooling water, etc.)	199,790,000		30.1
Total output	664,000,000		100.0

CHAPTER VIII

GAS PRODUCERS

As pointed out on p. 202, producer gas, the product of controlled primary combustion of coal with a thick fuel bed and with steam mixed with the primary air, is of increasing importance in industrial furnaces. Producer gas is the logical development of the "long-flame" combustion of fuels with suppression of primary combustion and increase of secondary. As in the case of coal-fired furnaces the steam is used to make possible the utilization of low volatile fuels and the gasification of all the combustible matter of the fuel and not merely of the volatile combustible. The gas producer represents the isolation of primary combustion under conditions of exact control, thus rendering it unnecessary to compromise in design and operation between the demands of the gas-producing apparatus and those of the furnace itself. Each may be constructed and run to the best possible advantage for its own purpose irrespective of the other. Consequently modern construction is to an ever-increasing extent discarding the direct use of coal in the furnace. For example, lime kilns fired with producer gas have been installed and are proving successful.

From the discussion on p. 202, it is obvious that a gas producer must operate with a thick fuel bed. The oxygen of the air burns to CO_2 extremely rapidly, raising the bottom of the fuel bed to a very high temperature. This temperature is lowered by the presence of the steam, largely due to its diluent effect, since the rate of interaction of steam with carbon is slow compared with that of oxygen and also since any hydrogen formed would be largely re-oxidized as long as oxygen is present, because of the high rate of this last reaction. As soon as the oxygen has disappeared, however, carbon begins to reduce both steam and CO_2 as indicated on p. 194. Because all these reduction reactions absorb heat the fuel bed is chilled thereby. There is therefore a sharp temperature gradient in the fuel bed, heat flowing rapidly by both

radiation and conduction from the lower layer of the bed (the oxidizing layer of CO_2 formation) up to this reduction zone. This tends to keep down the temperature of the oxidation zone, but that temperature will rise rapidly with increase of combustion rate, because the heat evolution due to increased CO_2 formation will be greater than can be dissipated to the reduction zone. Since, as will appear later, one of the most serious difficulties in gas producers comes from fusion of the ash, it is necessary to have the steam quantity high and the combustion rate low in order to keep down the temperature in the oxidation zone because this is the very point where the ash is being deposited. It is on this account that gas producers cannot in general be forced above a combustion rate of 20 lbs. of coal per sq. ft. of cross-section of fuel bed per hr., while with many coals with low-fusing ash, rates of 10 to 15 lbs. cannot be exceeded with safety.

Where the hot gas rises through the cold fuel the latter is distilled in the entire absence of air. If the temperature of this distillation is low, as is usually the case, large quantities of tar are formed, the removal of which is one of the serious problems of gas producer operation. Where the temperature is higher these hydrocarbons are cracked with formation of soot, almost equally obnoxious. Where the hot gas can be led directly from the producer to the furnace (raw producer gas) these impurities may not be a serious problem. The formation of this tar and soot can be eliminated by drawing the air down through the fuel bed but the mechanical difficulties encountered have in the past proven sufficiently serious so that this type of producer is not widely used.

The methane and traces of illuminants in producer gas come mainly from distillation of the fuel and are therefore highest in high-volatile, high B.t.u. coals.

From the discussion on p. 194, it is clear that a producer operated at low temperature will give relatively large quantities of CO_2 and less CO and hydrogen, in other words a low B.t.u. gas. The higher the temperature the greater the capacity of the producer and the higher the heating value of the product. Since the temperature of operation is limited by the temperature of fusion of the ash the value of a coal for gas-producer operation depends largely thereon.

Where producer gas is cleaned or piped any great distance it is cooled and the sensible heat of the gas is lost, while raw gas

is used directly and this heat conserved. The efficiency of conversion of the energy of the coal into heating value in the gas is therefore reported sometimes on a "cold," sometimes on a "hot" basis. It is convenient to use the cold basis as a standard for comparisons, even though where conditions warrant the additional sensible heat is recoverable.

Were no steam used in a coke-fired producer but the CO_2 completely reduced to CO the efficiency (cold) would obviously be 136,000/2(97,000) or 70 per cent (see p. 193). Were radiation eliminated, the 30 per cent heat loss would be the sensible heat in the gas. Steam reduces this loss by cooling the gas by the heat absorption of its decomposition, thereby increasing the efficiency. This reaction itself cannot cool the gases below the temperature at which it takes place at a reasonable rate but by using countercurrent flow of gas and fuel the gas cooled to this point can still be used to preheat the fuel so that the gas can leave the producer far below reaction temperatures. Incomplete reduction of CO_2 and steam, especially the latter, reduces the efficiency, because a large quantity of heat is used in vaporizing the water, and is not recoverable in practice. Volatile combustible matter in the coal greatly increases efficiency since it can be distilled at the expense of the sensible heat in the spent gases but increases trouble with tar. As a result of all these factors the cold efficiency of commercial producers is from 65 to 85 per cent, 70 per cent representing average practice.

While steam absorbs part of the heat of primary combustion and converts it into chemical energy due to the formation of hydrogen and monoxide, the facts that the steam is incompletely decomposed and that the heat content of the steam used is so great owing to its high heat of vaporization more than counterbalance the advantage gained. In consequence the cold efficiency of a gas producer decreases progressively as the steam consumption increases. It is therefore desirable to keep the steam consumption down to the lowest point compatible with prevention of fusion of the ash and maintenance of a reasonable rate of combustion in the producer.

It must be kept in mind that the fuel bed of a producer consists of four zones, the bottom layer of ashes the function of which is to support and insulate the incandescent fuel, the oxidation zone where the temperature is very high due to CO_2 formation,

the reduction zone where the temperature is low due to the heat absorption of decomposition of water and CO_2, and the preheating and distillation zone where the cold fuel is coked by the sensible heat of the gases from the reduction zone. It is obviously desirable to have the time of contact of the CO_2 and steam with the incandescent coke as great and to have the temperature of this reduction zone as high as possible in order to get high percentage decomposition into combustible gases.

The reduction zone gets its heat exclusively from the oxidation zone and consequently the top part of the reduction zone is at a temperature so low that the rate of the reduction reactions is very slight. Consequently it is unsatisfactory to try to secure time of contact by greatly increasing the depth of the fuel bed. It must be realized by increasing the cross-section of the producer, *i.e.*, by cutting down the velocity of the gases through the fuel bed and reducing the combustion rate. This reduces the distance between the oxidation zone where the heat is generated and the reduction zone where it is consumed and therefore facilitates the flow of heat from the first to the second. This increases the reduction of CO_2 and steam, because of the increase in both time of contact and temperature of the reduction zone. In this way it is possible to increase the heating value of the gas produced by 20 per cent and to increase the efficiency of the equipment by a corresponding though smaller amount.

It must not be concluded from the preceding paragraph that a gas producer should be operated with a thin fuel bed. The thicker the fuel bed, *other things equal*, the better the results because the greater the action in the reduction zone and the more complete the recovery of sensible heat in the distillation zone. The point is, that increase in time of contact obtained by increase in cross-section of the fuel bed is far more effective in increasing the efficiency of the reduction zone than a corresponding increase secured by greater depth.

The maximum temperature allowable in the oxidation zone of a producer is from 50 to 200° F. below the fusion temperature of the ash. The producer must be fired at a rate sufficiently low and with a steam to air ratio sufficiently high to keep the temperature down to this point. If the ash fuses at 2000° F. the combustion rate cannot exceed 5 to 6 lbs. of coal per sq. ft. of cross-section of the fuel bed per hr. without the use of an excess-

ive amount of steam which will result in a low efficiency and a low B.t.u. gas, rich in CO_2. A fusion point of 3000° makes it possible to more than double these combustion rates, reduce the steam-air ratio and increase the reduction, thereby increasing the efficiency. Therefore, while it is possible to make producer gas with fuels having low-fusing ash, the overhead expense of gas production is nearly double and the quality of the resulting gas lower, in comparison with a coal of high-melting ash. Where the wear and tear on the lining is the limiting factor (see p. 251), a very high-melting ash makes it possible to carry a heavy emergency overload for a short time, though at the expense of depreciation of the lining.

The great disadvantage of producer gas is its low heating value due to the large amount of diluent nitrogen and undecomposed CO_2. Gas with a heating value less than 90 to 95 B.t.u. per cu.ft. will not support its own combustion without preheating and such gas may all too easily be obtained from a producer because of difficulties which will be discussed under operation. An anthracite coal should give a gas of 130 to 135 B.t.u. and a good bituminous coal will easily produce 150 to 160 B.t.u. The highest grade bituminous coal in well-designed producers operated at reasonable combustion rates will give 180 B.t.u. continuously and has been known to yield 215 B.t.u. under special conditions. These excellent results can be realized, however, only where very complete decomposition of the CO_2 and steam is obtained, the CO_2 in the resulting gas being brought well below 5 per cent.

One of the major advantages of the gas producer lies in the fact that it can be designed and operated so as to handle low-grade fuels, either those with excessive ash (if non-fusing) or of low heating value (brown coals, lignites, etc.). In the latter case the heating value of the gas is lower. It is unfortunate that the combined water of these low-grade fuels is driven off in the distillation zone and cannot be utilized as the source of steam for the production of the gas in up-draft producers. The development of thoroughly successful down-draft producers would greatly increase the efficiency of decomposition of such low-grade fuels.

The apparatus for making industrial gas by these reactions is called a Producer, and consists essentially of:

1. A container or reaction vessel.
2. Provision for supplying fuel.

3. Provision for supplying air and steam.
4. Provision for removing ash.
5. Provision for removing gases formed.
6. Provision for removing flue dust and tar.

1. The Container.—The container is usually a steel cylindrical shell lined with fire brick. It may be of one stationary piece, or one piece rotating on a central axis, or in two parts, either or both of which may rotate. The top and other vulnerable points are generally water cooled. The size varies from 5 ft. diameter to dimensions of 10 and 12 ft., and the capacity is from 500 lbs. to 3500 lbs. coal per hr. The bottom may be a special shaking grate, but more frequently the fire bed rests upon a mass of ashes which is supported by a pan filled with water.

It is a well-known fact that steam has at high temperatures a selective disintegrating action on fire brick that is very serious. Also in a producer the fuel bed is continuously working downward and thereby abrades the lining. Furthermore the ash may exert a fluxing action on the lining even below its melting point (just as salt will melt ice below 0° C.) Consequently a producer lining operates under exceptionally severe conditions and the temperature of the oxidation zone must be held down to keep the deterioration within reasonable limits. The development of a special refractory to resist these conditions would make it possible to increase the efficiency and capacity of producers when using coals of high fusing ash.

2. Fuel Supply.—The supply of fuel may be intermittent or continuous; an intermittent feed is more simple from a mechanical point of view, but the spasmodic addition of large quantities of green coal leads to an irregular production of distillation gas and tar. It is all important that the top of the fuel bed be kept level and the mass of fuel uniformly distributed. There is a tendency for the larger pieces of the fuel to pass to the outside edge of the charge thus creating here a path of smaller resistance than through the center and causing irregularity of combustion. The blast of air and steam naturally takes the path of least resistance, and when a channel or "chimney" is once formed in the fuel bed, it rapidly increases in size owing to the localized combustion. This is fatal to good operation; first, the intense heat thus set free fuses the ash into masses of clinker very difficult to manage, second, much steam passes through so rapidly that it does not react with

the carbon and, leaving the producer at a high temperature, carries with it large quantities of sensible heat, third, uncombined air passes through these channels or blow holes and burns at the top of the fuel bed causing high CO_2 content and low calorific value in the gas. Provision for maintaining a bed of reacting fuel of uniform density free from such openings is a matter of importance and is accomplished more or less successfully in a number of ways which will be discussed later.

Coal broken to a uniform size of from 1 to 2 in., and freed from dust is the most desirable size of fuel, although "run of mine" when crushed to pass a 4-in. mesh or ring is the most common in use. It seldom, if ever, pays to use strictly slack coal even though the first cost be very low. The capacity of the apparatus is cut down by the choking of the blast, which must be driven at a higher pressure to force it through the fire. Blow holes are on this account more readily formed and a hot gas of low calorific value produced. Suction producers are generally fed with anthracite coal, for although a great deal of work has been done towards utilizing soft coal, the high ash, sulphur, and coking characteristics have until recently prevented its successful use. Western lignites in large sizes and German brown-coal briquettes give very good results. Bituminous coals work well in pressure producers and consequently anthracite is burned only in comparatively small plants of this class.

3. Supply of Air and Water Vapor.—Gas Producers may be divided into two types according to the method of supplying air and steam; in the first they are drawn through by means of an exhauster or other form of suction, and in the second they are forced through by pressure from a blower or injector. The former are used chiefly to supply internal combustion engines where the vacuum of the cylinder is directly communicated to the producer. In such cases provision is made for completely saturating the air with moisture in an independent apparatus, in which the temperature of the saturating water can be controlled.

In pressure producers the steam supply is usually under high pressure and is often used to inject the necessary volume of air into the fuel bed. It is desirable to be able to control the air fed to the producer and the ratio of steam to air independently of each other, since the first controls the combustion rate in the producer

while the second should be kept substantially constant for a given fuel but be capable of adjustment if the fuel changes. With a steam injector this control is impossible. The steam-air ratio can be maintained constant either by a thermostatic control inserted in the mixture and operating the steam valve, or by humidifying the air with hot water up to a thermostatically controlled temperature. The steam for direct injection or for heating the water can advantageously be obtained from the exhaust of the steam-driven air blower. The design of the distributing head is of great importance inasmuch as an even distribution of the air and steam supply is controlling in the operation of the producer. In those types in which the fuel rests upon a bed of ashes in a water-cooled pan, the distributing injector is placed in the center just below the zone of active combustion. Obviously suction producers must employ some form of grate so designed that the even distribution of the supply gases is insured. The formation of large clinkers is directly dependent upon the even distribution of this blast. Localized high temperature incident to blow holes and "chimneys" produces clinkers, difficult to remove from the ash bed. When this occurs on the edge of the fuel bed, they stick to the wall and may cause the fuel to arch across or "hang," thus greatly interfering with regular operation.

4. Removal of Ash.—In *suction* gas producers and others employing grates, the ash is removed by a movement of the grate bars. In order to compensate for the more easy passage of the supply gases at the area of contact between the fuel bed and the lining of the shell, the ashes must be somewhat more completely removed at the center of the mass than around the edge. In the various types of *pressure* producers the evolution from a stationary grate, through the rotating or otherwise movable exposed grate to grates submerged in water, and finally to the grateless bottom in which the ash stands in a pan of water accessible from every point of its circumference, has been slow but continuous. The periodical removal of the ash and clinker of necessity disturbs the fire zone and interrupts the production of a uniform gas. Hence most modern producers provide for either a large storage space for ashes, so as to render removal necessary only at long intervals, or for a continuous removal by working the bottom towards the outside edge and periodically lifting out the exuded portion by means of a plow.

5. Removal of Gas Formed.—The gas is generally removed through an outlet in the side of the top of the producer whence it passes to the coolers and scrubbers, usually through a water seal. Attempts have been made to withdraw the gas from the center of the producer below the upper level of the fuel bed in order to decompose the tar by cracking, but the mechanical difficulties encountered have resulted in the abandonment of this type.

6. Removal of Flue Dust, Soot and Tar.—Where the gas is to be used for operating an internal combustion engine, it must be cooled and purified from the dust of the ash, and the soot and tar which always accompany the decomposition of soft coal. Until very recent times coal tar of any description has not had ready sale unless from large installations, and the logical method of disposition was to return it to the body of the producer for further action, despite the fact that for many heating purposes highly carbonaceous material is particularly advantageous on account of the luminous flame produced and the radiant energy set free. The principles of removal of liquids and solids from gases are taken up in the chapter on Separation and their application here is obvious. The distribution of clean cold gas over wide areas can be done under low pressure (1 to 5 lbs.) and does not present difficulties of leaks or heat insulation. Condensation of tar is usually encountered on account of its incomplete removal. It is important to provide suitably located traps for it.

The application of the above general considerations in the design and operation of modern gas producers will be illustrated by a few of the large number of very efficient machines now available.

The Morgan producer consists of a stationary water-cooled top equipped with an automatic intermittent fuel door and an outlet for the gas. The shell is partly water cooled and rests upon a base with which it rotates while the fuel bed is supported by a layer of ashes held in a water-cooled pan. A spiral-shaped bar on the bottom causes the ash to travel to the outside rim where it is continuously removed by a plow. The fuel bed is kept level and compact by a heavy bar which floats on top of it and accommodates itself to any height, distributing the fresh fuel evenly and closing up blow holes. The blast is forced up under a central hood with cowl located in the ash bin. The working capacity of the unit is about 2000 lbs. of coal per hr.

The Chapman producer[1] uses a stationary shell located above a pan of water which serves as a water seal and which is so shaped that the ashes can be hoed out of it without difficulty. It is fed continuously with a ratchet-operated gear-tooth feed. The fuel bed is kept even and blow holes are closed up by a water-cooled rake, the prongs of which project into the fuel bed, so that, unlike

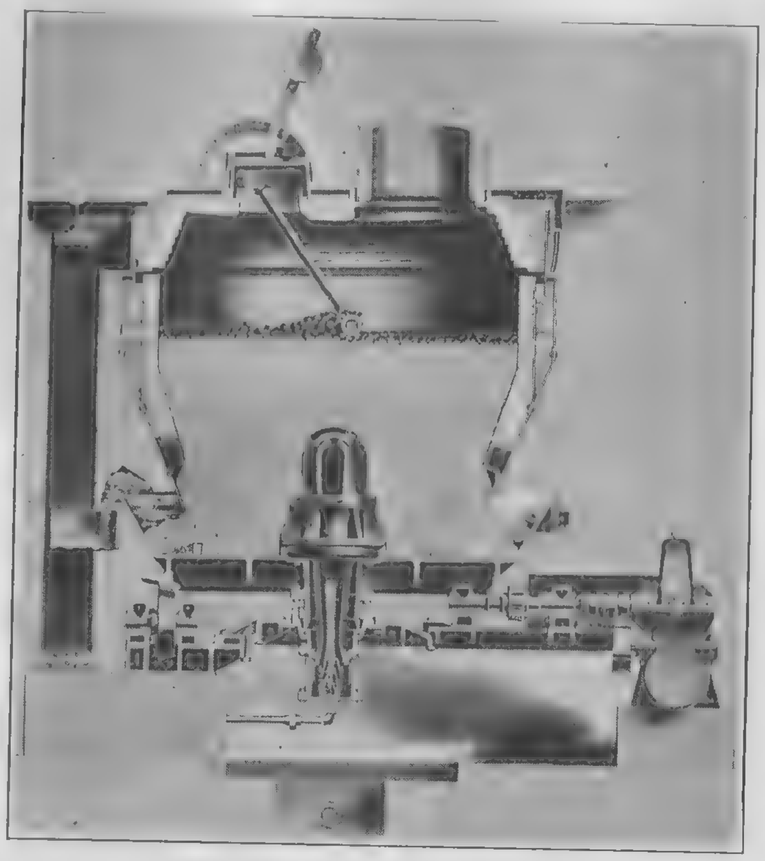


FIG. 59.*—Morgan Gas Producer.

the Morgan producer, holes are closed up by sidewise pressure rather than by having green coal raked into them.

The Smith producer consists of a series of rectangular sections side by side, each of which has its own grate and air supply. The grates slope backwards at an angle of 35° and mechanical stokers charge coal through the front wall, building up a single fuel bed

[1] See Fig. 60, p. 256.

* *Courtesy of Morgan Construction Co., Worcester, Mass.*

for the series of sections. Air, saturated with water vapor at a definite temperature, is drawn up through this bed by suction and the gas comes off through a central outlet and is cooled and cleaned before distribution.

The Hughes producer consists of a revolving brick-lined shell with a stationary water-cooled top carrying the charging doors and the exit for the gas, and an ash pan revolving with the shell. The fuel is leveled and the reaction mass kept free from channels

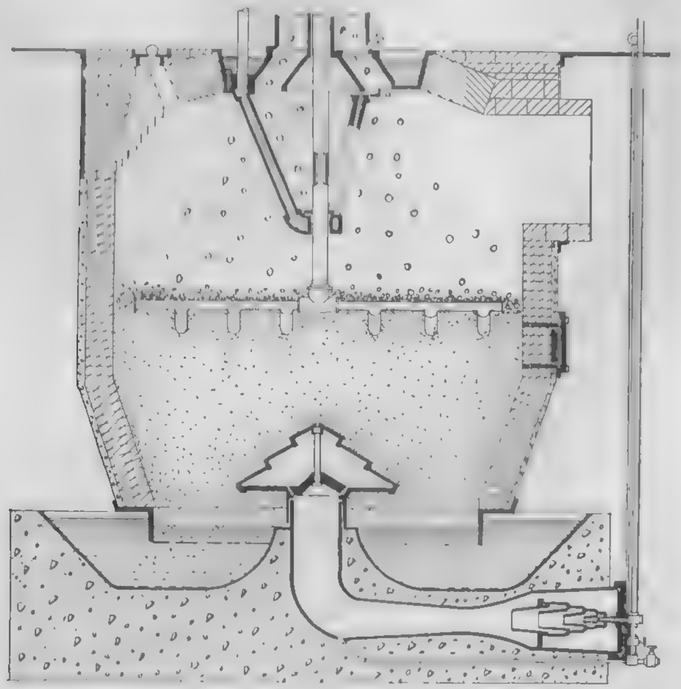


FIG. 60.—Chapman Gas Producer.

by a vibrating water-cooled poker depending from the stationary top, and reaching well into the incandescent zone. This poker swings backward and forward, and as the shell revolves it takes as a path a series of ellipses moving in an arc between the center and a few inches from the shell lining. The blast is introduced at the center through a bell-shaped distributing head. The capacity is about 2000 lbs. of coal per hr.

The Mond producer uses very large quantities of steam and low operating temperatures. The gas is consequently low in

heating value and high in CO_2. The advantage gained is that the destruction of the ammonia formed by distillation of the coal is avoided. The value of this recovered ammonia very greatly reduces the net cost of the gas. It is probable that the future will bring important developments along this line.

Gas Producer Computations.—Exactly as in the case of furnaces the performance of a gas producer is most easily controlled by gas analysis. A complete test on a producer set is time consuming and usually the equipment is so arranged as to make it difficult or impossible to secure all the data needed. It is therefore fortunate that the gas analysis alone can be made to give so much information.

It is often difficult to measure the amount of gas produced because the quantity is large and meters of sufficient capacity are not usually available and more particularly because the rate of gas production is liable to wide fluctuation. From the amount of fuel used, which can be determined readily and accurately, and a knowledge of the carbon content of the fuel, a carbon balance will immediately give the gas production, provided correction is made for the tar and soot formed and for any unburnt combustible in the ash. The latter is obtained from analysis of the ash but data on the former are difficult to secure accurately in a short test. Where a given fuel is used over a long period of time under reasonably constant conditions of producer operation, the tar and soot formed can be obtained directly from the plant records, expressing the result as percentage on the fuel, or better still as percentage on the total combustible matter fired. For coal from a given mine this figure will be quite constant; indeed for a given coal it will not change greatly even with wide variations in operating conditions.

Calculation of Gas Production.—The following illustration indicates the general method of computation of producer gas data. In the test chosen the gas production was measured directly and can therefore be compared with the computed result. In most industrial installations the gas cannot be measured with accuracy without undue trouble and expense, but the data used below can all be obtained without difficulty. Since the ultimate analysis of the coal was not available (as is usually the case) it was necessary to estimate its carbon content from its heating value. (See p. 190.)

Test 105, U. S. Bureau of Mines Bull. 13:		Data
Fuel:	Ash	11.41 per cent
	B.t.u (As fired)	10,528
	Sulphur	1.33 per cent
	Pounds fuel per hour	370.7
	Pounds tar per ton fuel	144

Gas analysis:	Per cent
CO_2	9.2
C_2H_4	0.4
CO	20.9
H_2	15.6
CH_4	1.9

Calculations

		C	H_2	O_2
CO_2	9.2	9.2	.....	9.2
C_2H_4	0.4	0.8	0.8	.....
CO	20.9	20.9	.....	10.45
H_2	15.6	....	15.6	.....
CH_4	1.9	1.9	3.8	.....
N_2	52.0	....	.....	.....
		32.8	20.2	19.65
O_2 from air	=			13.73
O_2 from steam	=			5.92
H_2 from steam	=		11.84	
H_2 from net H_2 in coal	=		8.36	

Call the weight per cent of carbon in the coal which goes into the gas $=x$.

Call the weight per cent of oxygen in the coal (total, except ash) $=y$.

Call the weight per cent of net hydrogen $=z$,

Assume tar to be $(CH_2)_n$, or 20.7 lbs. H and 123.3 lbs. of C per ton of coal. or 1.035 per cent H and 6.165 per cent C on the fuel as fired.

From the fact that $\frac{\text{carbon}}{\text{oxygen plus ash}}$ is $\frac{17{,}230}{16{,}750-\text{B.t.u.}}-0.98$,

$$(x+6.165)/(y+11.41)=1.79.$$

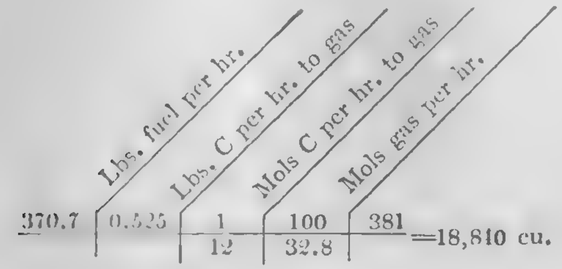
The ratio of carbon to net hydrogen in the gas, in mols, can be equated to the same ratio calculated from the coal:

$$\frac{32.8}{8.36}=3.823=\frac{x/12}{(z-1.035)/2.016}.$$

Also, assuming 1.2 per cent N in the coal,

$$x+6.165+z+\frac{18.02}{16}y+1.2+1.33+11.41=100.$$

From these three equations, $x=52.5$ per cent carbon in the coal which goes into the gas. Hence the gas per hour is:



The actual gas production per hour as metered was 18,170 cu. ft.

Estimation of Steam Consumption and Decomposition.[1]—Perhaps even more important than knowledge of the gas production is the determination of the steam consumption and of the extent of its decomposition in the producer. Under normal plant conditions the direct measurement of the steam used is almost as difficult as that of the gas produced, because the essential thing is the ratio of steam to gas and both these quantities are subject to wide fluctuation. Where a plant happens to be so equipped that the steam for a given unit can be fed to that unit as water, the measurement of the total amount of this water over a given period of time is easy. Where, however, resort must be had to steam meters of either the Orifice, Venturi or Pitot Tube type, these, even when of the integrating type, lose somewhat in dependability due to the excessive variations in operating conditions. It is sometimes possible to cool the gas below its dew point under such conditions as to measure the condensed water, although condensing tar makes this difficult. From this, correcting for the residual vapor in the saturated gas, one obtains the water vapor in the gas leaving the producer. This figure includes, however, all the water, both free and combined, in the fuel used, and very little of this is decomposed in the producer.

[1] See also p. 264.

The reaction rate equations developed on p. 204 can be used for estimation of the steam consumption and its percentage decomposition. It must be remembered that in the oxidation zone of the producer the oxygen goes almost quantitatively to CO_2 while the water vapor will be little reduced because any hydrogen formed would immediately be reoxidized. In the reduction zone this CO_2 and water vapor interact with the carbon in the way described on p. 246, the only difference being the presence of the diluent nitrogen and the fact that the initial CO_2 is high, while in the production of water gas it is zero.

It is well to remember that these equations mean simply this: that if steam is being reduced by carbon, any CO_2 mixed with the steam is also being reduced, and that, therefore, the ratio of reduction of the two depends only on their relative concentrations, and not on time of contact and temperature (except to a minor degree), since any change in these last two variables will have a similar effect on the reduction of both.

For computation it is best to use 100 parts of nitrogen as the basis because this gives an unchanging standard. On this basis call the parts of CO_2 v and of water vapor x as before, but remembering that the basis has changed. It will be seen that the differential equations are absolutely identical with those for the case of water gas, *i.e.*,

$$dv/d\theta = k_7x - k_2v \quad \text{and} \quad dx/d\theta = -(k_6+2k_7)x,$$

whence

$$dv/dx = \frac{\beta v - x}{\alpha x},$$

where

$$\beta = k_2/k_7 \quad \text{and} \quad \alpha = 2+(k_6/k_7),$$

which integrates into

$$(\beta-\alpha)v = x+[(\beta-\alpha)v_0 - x_0]\left(\frac{x}{x_0}\right)^{\beta/\alpha}.$$

For simplification assume that all the oxygen has gone to CO_2 at the top of the oxidation zone. Since air consists of 20.9 per cent oxygen and 79.1 per cent nitrogen this means that the CO_2 at the start of the reduction zone is 26.4 per cent on the basis of

100 N_2. Call the injected steam per 100 parts of nitrogen x_0. Inserting these values and remembering that the values of β and α should be the same as before, the following equation should represent the relation between the CO_2 content of the producer gas, steam used and the steam remaining undecomposed:

$$(1.01)v = x+(26.7-x_0)(x/x_0)^{1.319}.$$

If this equation be used to compute the CO_2 content of the gas by inserting into it experimentally determined values of the steam utilization and decomposition from gas producer tests, it is normally found that the calculated CO_2 value is lower than the observed one. There is general agreement that at the temperatures prevailing in the top of the fuel bed of a gas producer, particularly because of the catalytic action of the hot coal particles, the reaction,

$$CO+H_2O = CO_2+H_2, \quad \ldots\ldots\ldots \quad (8)$$

goes extremely rapidly in comparison with the reduction reactions discussed on pages 201 to 205. Furthermore, at these temperatures the equilibrium of this reaction lies toward the CO_2 side. In other words, this reaction causes the conversion of CO to CO_2, without, however, changing the total amount of reducing gas in the mixture. This increase of CO_2 at the expense of CO, not only in the upper zones of the fuel bed but in the gaseous space above it, has long been recognized. That part of it which occurs in the gaseous space above the fuel bed is called the Neumann reversion. The differential equations used above take no cognizance of this reaction and therefore give too low a value for the CO_2 content of the gas. Study of the results of a large number of producer gas tests indicate that the actual CO_2 percentage in the gas averages about 3.6 units above the values corresponding to this equation. Hence, the equation will give the relation between steam decomposition and the gas analysis if it be written in the following modified form:

$$\frac{101(\text{per cent } CO_2 \text{ in gas} - 3.6)}{(\text{per cent } N_2 \text{ in gas})} = x + (26.7 - x_0)\left(\frac{x}{x_0}\right)^{1.319}.$$

This equation offers a solution of the important problem of determining the steam consumption of a gas producer from analysis of the gaseous product, without the necessity of further data. The technique of using it will be made clear by a study of the accompanying table. The first seven columns give the

experimental results of the producer gas tests in question. The first six are the gas analyses and the seventh is the per cent steam decomposition as reported by the investigators. The remaining columns of the table represent the steps in computation necessary for the use of the above equation. Of the three runs reported, two are taken from Bone and Wheeler[1] and the last from Haslam, Mackie, and Reed.[2] The former used a high-volatile coal and the latter anthracite.

Column 8 shows the total atoms of oxygen appearing in the gas analysis, *i.e.*, twice the CO_2 plus the CO plus twice the O_2, if any. Column 9 gives the atoms of oxygen from the air, obtained by multiplying the nitrogen by the ratio 42/79. The difference between these two must be oxygen from decomposition of steam and is therefore numerically equal to the mols of hydrogen from this source as well as to the mols of steam chemically decomposed. The next column is found by dividing this by the fraction of nitrogen in the gas. It, therefore, represents the ratio of steam decomposed to nitrogen, or, in the nomenclature used above, x_0-x, where x_0 is the mols of steam per 100 mols of

	1	2	3	4	5	6	7	8	9	10	11	12	13
Run No.	Dry gas composition, per cent						Per cent steam decomposed reported	Atoms O in gas	Atoms O in air	Mols H_2 from steam	$x_0-x=H_2$ from steam over N_2	x_0 calculated	Per cent steam decomposed $\frac{x_0-x}{x_0}100$
	CO_2	CO	H_2	CH_4	N_2	O_2							
1	5.25	27.3	16.6	3.25	47.50	....	87.4	37.80	25.25	12.55	26.4	30.1	87.7
5	13.25	16.05	22.65	3.50	44.55	....	42.0	42.55	23.7	18.85	42.3	98.0	43.2
103	11.03	20.35	15.63	0.11	52.13	0.75	59.1	43.92	27.7	16.22	31.1	55.0	56.6

nitrogen in the entering air-steam mixture and x is that part of this steam which leaves the producer undecomposed. Designating the values of Column 11 as a, the equation may be rewritten in the form,

$$\frac{101\ (\text{per cent } CO_2 \text{ in gas}-3.6)}{(\text{per cent } N_2 \text{ in gas})}=x_0-a+(26.7-x_0)\left(\frac{x_0-a}{x_0}\right)^{1.319}$$

[1] *Jour. Iron Steel Inst.*, **73** (1907), 126.
[2] *Ind. Eng. Chem.*, **19** (1927), 119.

In this equation the only unknown is x_0; the per cent CO_2 is found in column 1, the per cent nitrogen in column 5, and a in 11. It can therefore be solved for x_0 by successive approximation. The results are given in column 12. Hence the per cent steam decomposition is computed by dividing column 11 by 12, giving the values found in column 13. Remembering that these values have been computed from gas analyses alone, they may now be compared with the results directly obtained by the investigators, found in column 7. It will be noted that the agreement is excellent.

This equation means that, as one increases the steam fed to a gas producer, the percentage of decomposition of that steam of necessity drops off and at the same time the carbon dioxide increases while the ratio of CO to H_2 decreases and the changes in these quantities make it possible to compute the change in steam injection necessary to produce them. Furthermore, if the gas analyzed be so collected that it is a truly representative average sample, the result thus computed should be the average steam consumption, irrespective of fluctuations in the steam-air ratio, provided these be not too large. Finally, the equation is more sensitive to changes in x_0 than to error in the CO_2 content; in other words, the percentage error in x_0 calculated by this means is apparently small. In the absence of the rather complicated set up necessary for making accurate direct measurements of steam consumption and decomposition in the producer, it is believed this equation offers a reasonably dependable means of estimating them.

Column 12 of the above table represents the mols of injected steam per 100 mols of nitrogen; since 26.6 mols of oxygen enter with this nitrogen, the volumetric ratio of injected steam to air is found by dividing the values of column 12 by 126.6. If one knows the carbon content of the coal employed and the per cent gasification of this carbon, the figures of column 12 can readily be converted into pounds of steam injected per pound of coal fired, a form more frequently employed in producer practice. Thus, if the molal ratio of injected steam to nitrogen be multiplied by the ratio of nitrogen to total carbon as shown by the gas analysis, it is converted into the ratio of mols of steam injected per atom of carbon gasified. Multiplying in turn by the ratio of the molecular weight of steam to the atomic weight of carbon gives

the pounds of steam per pound of carbon gasified and by the pounds of carbon gasified per pound of coal gives the required figure. The last run shown in the table was made with an anthracite containing 78.84 per cent carbon and because of the character of the coal its gasification was substantially complete. Hence, for this case the conversion becomes

$$\left(\frac{55}{100}\right)\left(\frac{52.13}{31.49}\right)\frac{18.02}{12}0.7884=1.08.$$

The investigators report a steam consumption per pound of coal of 1.03.

Another method of approach to the solution of this problem has been offered by Haslam,[1] who, from study of the results of a large number of gas producer tests under widely varying conditions has found that the constituents of producer gas approach an *apparent* equilibrium value.

$$K'=\frac{(CO_2)\ (H_2)}{(CO)\ (H_2O)},$$

dependent on the thickness of the fuel bed alone, and independent of gas velocity (rate of firing), the weight ratio of steam to coal, and the temperature of the exit gas. This empirical relationship is given by the equation:

$$K'=\frac{(CO_2)\ (H_2)}{(CO)\ (H_2O)}=0.096L,$$

where L is the depth of fuel bed in feet. While gas concentrations may be expressed in any consistent units, it is convenient to employ volumes per 100 volumes of dry producer gas.

This equation was derived from the data of Clements,[2] and Bone and Wheeler,[3] all in England, and from tests in the United States by Hunt, Johnson, and Willis.[4] The overall range of these data is shown in the following table:

[1] *Jour. Ind. Eng. Chem.*, **16** (1924), 782.

[2] J. Iron and Steel Inst. (London), 1923 (adv. proof), Engineering, Vol. 115, 597 (1923).

[3] J. Iron and Steel Inst. (London), Vol. 76, 126 (1907).

[4] 1923 Thesis, Mass. Inst. Tech.

Variable	Range	Ratio of Higher and Lower Extremes
Depth of fuel bed, feet	3.5 to 7.0	2.00
$K'=(CO_2)\ (H_2)/(CO)\ (H_2O)$	0.31 to 0.75	2.42
Gas temperature at outlet, deg. F.	1096 to 1481	1.35
Lbs. coal per sq. ft. of grate area	8.9 to 29.2	3.28
Steam, decomposed, per cent	40.4 to 87.4	2.17
Lbs. steam per lb. of coal	0.28 to 1.57	5.61
Undecomposed H_2O, per cent on dry gas	5.6 to 28.2	5.03
Per cent CO in dry gas	16.1 to 27.3	1.70
Per cent H_2 in dry gas	9.5 to 22.7	2.39

Thus most of the factors varied twofold, or more, but for the grades of coal used, only the depth of fuel bed was found to affect K'. The accuracy of the equation, $K'=0.096L$, is given as 10 per cent.

This method requires, in addition to the gas analysis, a determination of the moisture and combined oxygen in the coal employed, as well as a knowledge of the effective depth of fuel bed. With this additional data the equation can obviously be used for the determination of the steam injected. Attention should be called to the fact that the water term in Haslam's equation is not equal to x, as used above. x is that portion of the steam rising through the fuel bed which is not reduced in it, whereas the steam in Haslam's expression includes, in addition to x, the moisture and combined water of the fuel.

The quantitative relationship in a producer between the steam consumption, the rate of firing and the depth of the fuel bed has never been determined. From the explanations already given it is obvious that both an increase in the rate of firing and a decrease in the steam-air ratio run up the temperature in the oxidation zone. Since this temperature must be kept below the fusing point of the ash, a knowledge of the relation is important.

One can set up a heat balance on the producer from the bottom up to any particular section of the reducing zone. Consider 100 mols of entering nitrogen, corresponding to 26.6 mols of oxygen. At the oxidation zone, where this air first hits the hot coke, it will burn to CO_2. Call t the temperature at the section in question in the reducing zone. If the fuel bed be of adequate depth, the counterflow of the hot gases rising above this

section will preheat the coke flowing down to it substantially to the temperature t. The heat generated by combustion is partly consumed below this section in the reduction of CO_2 and water vapor, while the rest of it rises from the section into the upper part of the producer, partly as heat carried up by conduction and radiation through the incandescent fuel bed due to the temperature gradient through it, and partly as sensible heat in the gases. The heat flowing up through the section by conduction and radiation may be calculated by subtracting from the total heat available from combustion above the temperature level t the heat consumed by the reduction reactions taking place below that section, computed however on the assumption that they take place at the temperature t. This is allowable, since, although the reaction mechanism is entirely different, the net overall result is the same.

The heat of combustion of 26.6 mols of oxygen to CO_2 is 26.6 (97,000) = 2,580,000 C.h.u. or 4,640,000 B.t.u. To this must, however, be added the sensible heat content of the coke up to the temperature t, since the coke enters that part of the producer under consideration at this temperature level. The temperature in the active part of the reduction zone averages about 1700° F., and the average heat capacity of carbon up to this temperature is approximately 4.7 B.t.u. per pound mol. Taking the temperature t_a at which the reacting materials enter the producer as the base line, the heat brought in by the hot carbon consumed in the oxidation zone is 4.7 (26.6) $(t-t_a) = 125$ $(t-t_a)$. The total heat available above the temperature level t is equal to the sum of the preceding quantities less the heat content of the primary combustion products at this temperature. There are 100 mols of nitrogen with an average heat capacity (see p. 10) of about 7.4, corresponding to 740 $(t-t_a)$ heat units and 26.6 mols of CO_2 with a heat capacity of about 11.5, corresponding to 305 $(t-t_a)$ heat units. There are also x_o mols of steam which entered with the air; its heat capacity averages 9 (see p. 10) and its heat content, 9 $x_o(t-t_a)$. The algebraic sum of these quantities is $2{,}580{,}000-(920+9\ x_o)(t-t_a)$. The heat consumed by reduction with carbon is due partly to reaction of CO_2 and partly to steam. Per mol of gas reduced, the former consumes about 38,000 C.h.u. *at the temperatures of the reduction zone* (somewhat less than at room temperature) and the latter

about 30,000. The relative reduction of the two obviously varies from case to case, but if one will employ an average heat of reduction of 34,000 C.h.u., one can, without serious error, speak of the total reduction of the two gases combined.[1] Designating the initial CO_2 plus steam as z_0 and the sum of unreduced CO_2 and steam at the section in question as z, the total reduction is obviously z_0-z. Furthermore, $z_0=26.6+x_0$. The heat consumption of these reduction reactions is therefore 34,000 (z_0-z). Consequently, per 100 mols of nitrogen entering the bottom of the producer, the residual heat flowing up by conduction and radiation through the section under consideration is $2{,}580{,}000-(920+9x_0)\ (t-t_a)-34{,}000\ (z_0-z)$ C.h.u. Calling r the amount of nitrogen rising per hour per square foot of cross-sectional area of the producer, expressed as hundreds of mols, the conduction heat current flowing upward through the section involved is

$$\frac{Q}{A\theta}=r[2{,}580{,}000-(920+9x_0)\ (t-t_a)-34{,}000(z_0-z)], \text{in C.h.u.} \quad (1)$$

$$=r[4{,}640{,}000-(920+9x_0)\ (t-t_a)-61{,}200(z_0-z)], \text{in B.t.u.,}$$

where in the first expression degrees Centigrade are employed and in the second, degrees Fahrenheit.

The equation is on a basis of 1 sq. ft. of cross-section of the producer and 1 hr. This heat current may be equated to the thermal conductivity of the fuel bed times the temperature gradient, *i.e.*,

$$Q/A\theta = a\,dt/dL \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

This is allowable, despite the fact that much of the heat flows by radiation, if the coefficient a, be empirically chosen for the temperature range in question (see pp. 167 to 168). Furthermore, since the reduction rate of the two gases is roughly the same but the reaction rate increases in the usual way, geometrically with increase in temperature, one may set up the reaction rate expression,

$$r\,dz/dL = -kze^{bt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The exact solution of these equations, even if possible, would be complicated. For an approximate solution it is perhaps allowable to give an average value in each specific case to t in Eq. (1), *i.e.*, to write,

[1] This is satisfactory provided the CO in the resulting gas exceeds the H_2 from decomposition of steam. This is always the case unless excessive quantities of steam are used.

$$B = 2{,}580{,}000 - (920 + 9x_0)\left(\frac{t_0 + t_1}{2} - t_a\right) - 34{,}000\ z_0. \quad .(1b)^1$$

With this approximation the solution is as follows:

$$e^{bt_0} - e^{bt_1} = \frac{br^2}{ak}\left[B\ln\frac{z_0}{z_1} + 34{,}000(z_0 - z_1) \right], \quad . \quad . \quad . \quad . \quad (3)$$

where the subscript 0 indicates conditions at the border line between oxidizing and reducing zones and 1 corresponds to the end of the reducing and beginning of the distillation zone.

For normal conditions of producer operation with adequate depth of fuel bed, the second term on the left-hand side of Eq. (3) is negligible in comparison with the first, rarely amounting to 5 per cent of it. It is, therefore, advisable to drop it and rewrite the equation as

$$e^{bt_0} = Kr^2\left[B\ln\frac{z_0}{z_1} + 34{,}000(z_0 - z_1) \right]. \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

The constant b is approximately 0.006 to 0.007 (see below); K is best determined from data on the coal in question, or at least on a coal of similar type as to coking quality and texture of the ash.

The qualitative interpretation of this equation is instructive. The left-hand side rises rapidly with temperature, but the rate appears on the right-hand side as a square term. Consequently, while the working rate (*i.e.*, capacity) of a producer increases with the temperature, its increase is less rapid than the ordinary increase of reaction rate for a given increase in temperature of the oxidation zone. This is because the average temperature of the reducing zone is far below that of the oxidizing zone and rises less rapidly than it. Furthermore, for a given increase in temperature, *i.e.*, for a given increase in the left-hand side of this equation, one gains a double advantage, namely, improvement in both capacity and amount of decomposition of the steam and CO_2. Within certain limits one can, by changing the steam-air ratio, use this advantage for either purpose. Since the rate term appears as a square while the decomposition term is the first power, it is obvious that increase in temperature is more effective in securing complete decomposition than greater capacity. Producer experience bears out this conclusion.

[1] This expression assumes temperatures in °C.; if °F. be used it is necessary to multiply the first and last terms on the right-hand side by 1.8.

The useful work done in the reduction zone of a gas producer is the reduction of $z_0 - z_1$ mols of CO_2 and water vapor to combustible gas. The numerical value of this expression is obviously found from the gas analysis by taking the sum of columns 2 and 10 of the table on page 262 and dividing by the *fraction* of N_2 in the gas. Under comparable conditions of operation it is surprising how constant is this quantity. When using a cold air-steam mixture it averages around 30, seldom deviating more than 10 per cent from this figure. The data indicate that, as one would expect, the reduction falls off slightly with increasing steam-air ratio. Preheating of the air greatly increases $z_0 - z_1$. Thus, Bone and Wheeler, using about 30 mols of steam per 100 of nitrogen with air preheated to about 250° C., obtained values of $z_0 - z_1$ of 42, whereas Haslam, under comparable conditions, without preheat other than that due to the steam, realized only 31. His steam-air mixture entered at about 80° C. Equation (1) can be used to estimate what the increase ought to be, since decrease in the temperature term secured by increasing t_a should give a corresponding increase in $z_0 - z_1$. In other words, calling the increment in $z_0 - z_1 = \Delta z$.

$$\Delta z = -\frac{920 + 9x_0}{34{,}000}\Delta(t_1 - t_a), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Bone and Wheeler used a much deeper fuel bed than Haslam and were thereby able to cool their gases approximately 100° C. lower. Their net temperature gain was, therefore, $250 + 100 - 80 = 270°$. Hence, from the above expression, Δz should be 9.5, as compared with the 11 actually realized. This emphasizes the great value of preheating the steam-air mixture in increasing the cold efficiency of the producer.

From a study of the data available, it seems that the reduction realizable in a producer may be estimated with reasonable precision by the expression,

$$z_0 - z_1 = 54 - 0.04x_0 - 0.018\ (t_1 - t_a). \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It must, however, be kept in mind that this assumes a fuel bed of adequate depth, properly operated to maintain uniformity. Where one finds total reductions much lower than indicated by this expression, one is probably faced with poor fuel bed conditions. In using Equation 5, one must also remember that the deeper the fuel bed the lower t_1, although with reasonable depths

the variation in t_1 is not great. It is seldom above 800 or below 600° C.

All these expressions are based upon a given amount of air entering the producer (126.6 mols, equivalent to 100 mols of N_2). The underlying reason for this basis is that the heat supply and hence the performance of the unit is determined by the rate of combustion and this in turn by the air supply. Firing rate need not be and in general is not constant; one need only make sure that there is never an inadequate amount of fuel on the hearth, although in the end this of course implies that average firing rate is approximately proportional to the average rate of air supply.

Considerable data on fuel bed temperatures have been reported by Haslam and his associates.[1] Analysis of these data indicates that, in the temperature range of the reducing zone, the constant b lies between 0.006 and 0.007. Accurate measurement of temperature conditions in a producer bed is, however, very difficult. While in a carefully operated producer, conditions are reasonably uniform across any section taken near the top of the fuel bed, at the bottom, in the oxidation and hotter portions of the reduction zones, this is by no means the case.

In and just below the oxidation zone it is impossible to avoid localized packing of ash and partially burnt-out fuel. Consequently, the entering air rises rapidly through some portions of the bed and far more slowly through others. The former are equivalent to little producers within the main unit operating at higher firing rates and hence at far higher temperatures. Because of this, there are wide temperature fluctuations at any given level of the lower portions of the bed. Thus, at a given level, just above the oxidation zone, where the air rate is low, one will find a low temperature, whereas at a point a little to one side one may find a much higher temperature further up in the producer. Differences in gas composition at a given level will, however be far less than differences in temperature. The hot chimneys are still functioning as gas producers, although at operating rates far higher than the average. Now, t_0 in Eq. (3) is the temperature of the oxidation zone, *i.e.*, the maximum temperature existing in the fuel bed. It is vitally important, because it determines the capacity limit of the producer without developing

[1] Haslam, Mackie, and Reed, *Jour. Ind. Eng. Chem.*, **19** (1927), 119. Haslam, Ward, and Mackie, *Jour. Ind. Eng. Chem.*, **19** (1927), 141.

clinker trouble, but in measuring it directly one must remember that the point of maximum temperature may be found first at one level in the producer bed and later at another.

The utility of Eq. (3) may best be illustrated by applying it to certain of Haslam's data. He reports a run with a coal containing 78.84 per cent carbon, using 0.413 lb. of steam per pound of coal, firing at the rate of 9.72 lb. of coal per square foot of grate area per hour, yielding a gas containing 7.88 per cent CO_2, 0.10 per cent O, 23.4 per cent CO, 8.72 per cent H_2, and 59.9 per cent N. In this operation he found a maximum fuel-bed temperature of 1900° F. His entering air-steam mixture may be assumed 100° F. and the top of his fuel bed, 1200°. Using $b=0.007$, compute the value of K for this coal. The following tabulation will be self-explanatory.

		C	O_2
CO_2	7.88	7.88	7.88
O_2	0.10	.....	0.10
CO	23.40	23.40	11.70
H_2	8.72		
N_2	59.90		
	100.00	31.28	19.68
O_2 from air $=59.9\frac{2}{7\,0}=$			15.93
O_2 from steam, difference $=$			3.75
H_2 from steam $=$			7.50

$$\frac{\text{lb. st/lb. C.}}{0.413}\Big|\frac{\text{mol. st./atom. C.}}{0.7884}\Big|\frac{12}{18.02}\Big|\frac{31.28}{0.599}=18.24 \text{ mols steam/100 } N_2=x_0.$$

$$\frac{\text{Atoms C/hr./sq. ft.}}{9.72\ (0.7884)}\Big|\frac{0.599}{12}\Big|\frac{31.28}{}=0.0122=r=\frac{N_2/\text{hr.}}{100}.$$

$$CO_2/100\ N_2=7.88\left(\frac{100}{59.9}\right)=13.15$$

$$x_0-x_1=7.50\left(\frac{100}{59.9}\right)=12.52$$

x_1, by difference $=5.72$

$z_0=26.6+18.24=44.84.$

$z_1=13.15+5.72=18.87.$

$z_0-z_1=\quad 25.97$

$$B=4{,}640{,}000-\Big(920+9\ (18.24)\Big)\left(\frac{1900+1200}{2}-100\right)-61{,}200\ (44.81)$$

$$=332{,}000.$$

Inserting these values in Eq. (3*a*), $K=2100$.

Let it be required to increase the firing rate of this producer by blowing with air 9.7 times as fast as at present, using, however, a steam-air ratio only 90 per cent as great. (These figures are chosen because Haslam actually conducted such an operation.) What maximum temperature would one anticipate in the fuel bed under these new and more drastic conditions?

The reduction, z_0-z_1, obtainable is computed by the use of Equation 5 on page 269. Otherwise, the tabulation below should be self-explanatory.

$$r=9.7(0.0122)=0.118.$$

$$x_0=0.90(18.24)=16.4$$

$$z_0=26.6+16.4=43.0$$

$$z_1-z_1=54-0.04(16.4)-0.018(1200-100)=33.7$$

$$B=4{,}610{,}000-\left(920+9\ (16.4)\right)\left(\frac{2600+1200}{2}-100\right)-61{,}200\ (33.7)$$

$$=95{,}000.$$

The term $t_0=2600$ in B is estimated. Inserting the values in Eq. (3*a*), one obtains $t_0=2570°$ F. Haslam actually found a temperature of 2600°.

To emphasize the effect of changing steam-air ratio, compute the maximum temperature of the fuel bed, first, for an air rate 3.9 times that of the original experiment, with a steam-nitrogen ratio of 0.175, the steam-air mixture entering at 150° F. and the gases at the top of the fuel bed being at 1450°, and second, for conditions otherwise the same except that 2.8 times as much steam is used and the top of the fuel bed was 1300°. Under the first conditions, computed as before, $z_0-z_1=29.9$, $z_1=14.2$, $B=80{,}000$ (if t_1 be assumed 2300), whence, from Eq. (3), $t_0=2290°$. Haslam found 2400 under these conditions. Similarly, with 2.8 times the steam, $x_0=49$, $z_0=75.6$, $z_0-z_1-31.3$, $z_1=44.3$, $B=-2{,}100{,}000$ (assuming $t_0=2150$), whence, from Eq. (3), $t_0=2170°$. The temperature as actually measured was 2200° F.

It will be noted that in each case in computing B one must estimate t_0. If the final value of t_0 thus computed does not check this estimate, the computation must be repeated. However, in the equation for B, a small error in t_0 makes little difference.

The figures emphasize the fact that oxidation-zone temperature comes down far more rapidly with drop in firing rate r than with increase in steam-air ratio x_0. None the less increasing steam is a potent means of increasing capacity without encountering clinkering troubles.

CHAPTER IX

CRUSHING AND GRINDING

OBJECTS OF CRUSHING AND GRINDING

When a solid body is subjected to chemical change from without, the action producing such change is confined to the surface of the solid, and the rate of the reaction is a function of the surface exposed. In order, therefore, to complete a reaction in a minimum time, the area per unit weight or volume must be made as large as possible. This object is accomplished by first crushing the solid to small pieces, and then grinding these to a very fine powder. This relationship between the area exposed (as determined by the size of the particles) and the rate of reaction plays an important part in many industrial processes. Examples are seen in the solution of solids in liquids; in the interaction of two solids, as in the production of cement clinker; in reaction between solids and gases, as in the combustion of pulverized coal; and in the chemical reactions which result in the setting of Portland cement. The physical properties, also, of a material may be profoundly influenced by its state of division; for example, the covering power of pigments.

If, however, the solid be not homogeneous, a second object which may be attained in crushing, is the detaching or cleaving of one mineral or constituent from another closely associated with it. In some cases, a satisfactory breaking apart is accomplished by relatively coarse crushing, as for example the parting of coal from slate. On the other hand many mineral ores require very fine grinding to effect a complete separation of one constituent from the others. The concentration of the valuable constituent of a raw material from the gangue or worthless portion by subdividing and then separation is generally spoken of as "ore dressing" and forms a very important step in many industrial chemical processes.

Occasionally the primary object of a grinding operation is mixing, as in the grinding of certain pigments in oils.

TOTAL SURFACE

The relationship between the area of a particle and its linear dimension may be obtained by considering one unit volume of any material made up of individual particles of uniform size and having a linear dimension (diameter, side, etc.) L. The area of each particle is KL^2 and its volume is kL^3, the constants K and k depending upon the shape of the particle. The total number of particles per unit volume is

$$\frac{1}{kL^3}$$

Since the area of each particle is KL^2, the total area A is

$$A=\frac{KV}{kL},$$

where V is the total volume. If the density (weight per unit volume) of the substance is G, the volume may be expressed by its total weight W divided by the density, and the total area becomes

$$A=\frac{KW}{kLG}.$$

If the particles have the shape of a cube, K becomes 6 and k equals 1; if a sphere, K is π and $k=\frac{\pi}{6}$. Hence, for either cubes or spheres, $K/k=6$. This value is generally used for all shapes.

It is, however, unnecessary to know the value of these constants in order to compare the relative effective areas of *equal weights* of any material when existing in two states of subdivision. The dimension L may be determined by passing the material through a series of sieves of known apertures, and by assuming that the average dimension of the particles remaining on any sieve is the mean value of the *actual* dimensions of the sieve which just passes them, and that of the next sieve which they fail to pass. While the numerical value for the area will, of course, depend upon the values of the constants chosen for the material under consideration, the *relative* values will be independent of these constants. This assumes that the average shape remains the same. That is, the area A_1 before grinding the particles of dimension L_1 is

$$\frac{K}{kL_1};$$

and after grinding to dimensions L_2 is

$$A_2=\frac{K}{kL_2}.$$

Therefore,

$$\frac{A_2}{A_1}=\frac{L_1}{L_2},$$

for equal weights of material.

Obviously a mass may be subdivided in either of two ways.

1. A force may be applied to it greater than its breaking strength, so that it is crushed and split, or
2. The mass may be cut or torn apart.

The final result in either case is an increase in the surface of the mass.

Rittinger's law assumes the mechanism of subdivision to be essentially that of shearing, and that the energy consumed is proportional to the fresh surface produced. Since the total surface per unit weight is inversely proportional to the size of particle, the work done in reducing a given amount of material, E, is

$$E=C\left(\frac{1}{L_2}-\frac{1}{L_1}\right),$$

where L_1 is the initial and L_2 the final linear dimension of the individual particles; C depends on the characteristics of the material and on the type and method of operation of the apparatus. Thus, if 10 H.P. hours be required to crush a given weight of a certain material from 2 inches to 1 inch, the work (E_2) required to crush from 1 inch to $\frac{1}{2}$ inch may be calculated as follows:

$$\frac{E_2}{10}=\frac{C\left(\frac{1}{0.5}-\frac{1}{1}\right)}{C\left(\frac{1}{1}-\frac{1}{2}\right)},$$

whence $E_2=20$ H.P. hours. If the particles are small (below 6 mesh), the energy actually required to crush a material is

generally smaller than that calculated by this equation. Owing, probably, to incipient fractures resulting from previous crushing, subdivision takes place more readily than it otherwise would.

Kick's law assumes the energy required for subdivision of a definite amount of a material to be the same for the same fractional reduction in average size of the individual particles. Thus, if 10 H.P. hours be required to crush a given weight of a certain material from 1 inch to $\frac{1}{2}$ inch, the energy required to reduce it from $\frac{1}{2}$ inch to $\frac{1}{4}$ inch or from $\frac{1}{4}$ inch to $\frac{1}{8}$ inch, etc., would be the same. Mathematically expressed, Kick's law becomes

$$E = b \log \frac{L_1}{L_2},$$

where b is an experimentally determined coefficient.

This coefficient depends on the type of crusher employed, as well as the character of the material. This relationship can be derived if one assumes that each particle is crushed by direct pressure, that the crushing strength per unit area is constant, and that a given particle whatever its size, upon breaking forms a definite number of smaller particles of shape similar to the original. This law is inexact, especially for coarse crushing.

Neither Rittinger's nor Kick's equation represents the facts accurately and it seems probable that a satisfactory expression, when it is developed, will lie between the two.

SELECTION OF MACHINES

The selection of machines for crushing and grinding usually depends on three factors:

1. Physical properties of the material to be ground.
2. The size of the feed and product.
3. The total tonnage to be ground and other local conditions.

1. Physical Properties of the Materials.—The selection of proper machines for crushing and grinding is greatly affected by

(*a*) The hardness of the material to be ground.
(*b*) Mechanical structure of the material, that is, whether brittle, or fibrous and tough, or soft or whether it softens when warm, etc.
(*c*) The moisture content.

(*a*) *Hardness.*—The meaning of the words "hard" and "soft" is entirely relative, yet the materials which require subdivision in order to prepare them for further operations may be divided roughly into these two classes. The scale of hardness employed in mineralogy is utilized in this connection, and is as follows:

1. Talc, Soapstone.
2. Rock Salt, Gypsum, Pure Graphite, Soft Coal, etc.
3. Calcite, Burnt Lime, Marble, soft grades of Limestone, Chalk, Hydraulic Limestone, (Common) Cement, Barytes, etc.
4. Fluorite, Magnesite, Soft Phosphate, Limestone, etc.
5. Apatite, Hard Phosphate, Hard Limestone, Chromite, etc.
6. Orthoclase, Feldspar, Magnesite, Hornblendes, etc.
7. Quartz, Granite, Ores, Sandstone, etc.
8. Topaz, etc.
9. Sapphire, Corundum, Emery, etc.
10. Diamond.

Materials up to and including class 4 are designated as "soft" while those in the higher classes are termed "hard." A rapid method of approximating hardness is to cut the material under examination with a knife or to scratch ordinary window glass with it. If it can be whittled easily like chalk, it is "very soft." Marble and many hydraulic limestones can be cut quite easily and would be classified as soft. Magnesite and phosphate rock can be easily scratched but will not scratch glass and are termed medium. Beyond this line, little impression can be made with a knife and the materials may be classified as very hard.

Hardness not only affects the size and design of the machine in order that it may have sufficient strength to crush the material, but as the material increases in hardness its abrasive action increases and the machine must be designed so as to provide the fewest possible wearing parts. Furthermore, in grinding abrasive materials a machine not only should have few bearings but these should be protected from dust in a proper manner. Also, in grinding abrasive material, low-speed machines require much less maintenance than do the high-speed machines. In general

low-speed grinding machines should be used when the per cent of quartz in an ore is higher than 4 or 5 per cent.

(*b*) *Mechanical Structure.*—If a material is of a fibrous nature it cannot be crushed by pressure or shearing action, but must be torn apart. While both coal and wood are soft materials, they require radically different types of machines for disintegrating them, on account of the fact that the wood is of a fibrous nature and must be cut or torn apart. Machines for subdividing such fibrous materials as wood, bark, etc., are often called distintegrators.

(*c*) *Moisture.*—Moisture plays an important part in the selection of crushing and grinding machinery. If the moisture is more than 4 or 5 per cent the material becomes sticky or pasty and under such circumstances it is extremely difficult to maintain free crushing.[1] On the other hand, after the moisture content exceeds about 50 per cent, the material is quite fluid and under such circumstances the water may actually be used to aid free crushing by washing and carrying away the finely ground product. It is apparent that moisture affects the pastiness of fine material more readily than it does coarse material. Therefore, while some mills cannot handle material containing more than 3 or 4 per cent of moisture, others work best when the moisture content is over 55 or 60 per cent.

2. Fineness.—Fineness governs the selection of machines in two ways:

(*a*) The size of feed.
(*b*) The size of product.

Some machines from their very design can handle only coarse material, while others can handle only fine material. Some machines produce a very uniform product, that is, all of the particles are close to a given size, whereas others, by virtue of their construction, produce a product with considerable variation in size. There is frequently a lower limit to the size of the particles desired in the product. Thus in crushing pyrites for making sulphuric acid very fine material is not desired. Also, in grinding malt, or any substance to be leached, very fine subdivision is undesirable. In such cases, machines must be selected that produce a minimum amount of fine material.

[1] See p. 280.

3. Tonnage and Other Local Conditions.– Tonnage is a vital factor in determining the economic balance between fixed charges (interest, depreciation and taxes) and operating costs (labor, power and maintenance). The greater the tonnage, the more money may be spent for the initial installation in order to cut down such operating costs as power and maintenance. Interest and depreciation must be balanced against power, labor and maintenance, and the greater the tonnage the more necessary it is to use machines whose *operating* costs are low.

In addition to tonnage, there are always a number of local conditions which affect the selection of machines. For example, in certain mining fields only those machines which can be demounted and easily freighted by pack animals are purchased. Every situation has local peculiarities that must be given due weight.

CLASSIFICATION OF MACHINES

Machines may be classified in two ways, either by the size of feed, or by the method of applying the breaking force. In considering the crushing and grinding machines, it is obvious that any one machine will operate efficiently only between certain size limits. One should not drive a tack with a sledge or a spike with a tack hammer. A single machine will not crush economically from a very large to a very small dimension, and hence crushing and grinding machinery is divided into the following classes:

I. *Preliminary breakers,* which crush pieces having a maximum dimension of 2 to 60 in.
II. *Intermediate crushers,* which will take a feed of about $1\frac{1}{2}$ to 2 in., and produce a product of about $1\frac{1}{4}$ to $\frac{1}{2}$ in. diameter.
III. *Fine crushers,* which will take a feed of from $1\frac{1}{2}$ to $\frac{1}{2}$ in., and produce a product that will pass through a 10-mesh[1] screen.
IV. *Fine Pulverizers* which will take a feed of from $\frac{1}{2}$ to $\frac{1}{4}$ in. and produce a product as fine as 200-mesh.

[1] Ten openings to the linear inch when using a standard wire. See also p. 308.

In addition to the above four classes, there is a class known as shredders or disintegrators, designed to handle fibrous and brittle material.

It will be noted that in the above classification there is an overlapping in the range that these machines will handle, and it must be remembered that the above classification is not rigid.

Crushing and grinding machines may also be classified into three principal groups according to the method of applying the breaking force.

1. Those which break from a continued pressure.
2. Those which break from impact or direct blow.
3. Those which break by abrasion or grinding through a shearing force.

In general it may be said that the first is best adapted to coarse crushing while the other two, either singly or combined, are employed for fine crushing and pulverizing.

Free Crushing.—Before discussing individual machines it is necessary to call attention to a basic principle in all operations involving the reduction of size, and one which is of the utmost importance in the design and operation of crushing and grinding machinery, namely, that of "free crushing." In order that the breaking force, however applied, may be efficiently used, and in order that the maximum capacity of the mechanism employed may be obtained, it is essential that each particle be removed from between the crushing surfaces as soon as it has reached the dimension desired. Fine material, by remaining between the moving surfaces, cushions the material to be broken, absorbs a large portion of the energy expended, cuts down the output of the machine, and increases the percentage of the so-called "fines," which is that portion smaller in diameter than the size desired. The opposite of "free crushing" is known as "*choke feeding*." Particular attention, therefore, should be paid to the design of crushing and pulverizing machinery to insure a free discharge of the fine material and its complete removal from the zone of reduction.

The rapid removal of product which aids free crushing may be accomplished, in general, in three ways:

1. By the use of water to wash out fine particles.
2. By the use of air to blow them out.

3. By the use of centrifugal force, which may be applied in various ways, as will be noted under the discussion of the various types of machines.

Open or Closed-circuit Operation.—There are two general methods of crushing and grinding, the "Open Circuit" and the "Closed-Circuit Method." In the open circuit, all the material discharged by a machine goes on through the system. In the closed-circuit method, as fast as any of the product reaches the desired size it is screened and removed. The oversize particles are recirculated through the machine until they reach the desired size and are then removed. In the open-circuit method initial cost of installation is low, but the power cost per ton of output is high. The closed-circuit system should be used on all large scale installations on account of the uniformity of the output and the low cost of power.

For closed-circuit operation it is advisable to regulate each mill so that it delivers a product much of which is oversize. If the scale of installation warrants, it may be advisable to use one size of machine for grinding the main output and another for regrinding the oversize particles or tails, since these average smaller than the original feed and therefore require a different mill setting for best results.

Since there are usually two or more machines in series and since each unit produces a certain amount of material finer than the normal product of the next unit in the series, capacity can be increased and power consumption reduced by screening out these fines and having them by-pass the next unit in the series. As a result, the load on the mills is reduced, the cushioning effect of fines is diminished and the product is more uniform.

I. PRELIMINARY BREAKERS

There are two types of preliminary breakers which handle material from 2 to 60 in. in diameter, the first being Jaw Crushers, and the second, Gyratory Crushers. Both these machines break with a continuous pressure. Jaw Crushers employ a reciprocal motion and are intermittent in action, whereas in Gyratory Crushers this reciprocal motion is combined with a rotary motion and the action is continuous.

Jaw Crushers.—Jaw crushers, which break material by squeezing it between a fixed and a movable jaw, may be considered as of three types according to the movement of the jaw. First, those which have the movable jaw pivoted at the top and which therefore have the greatest movement and crushing action at the point of *egress*. Second, those pivoted at the bottom and which therefore have the greatest movement and crushing action at the point of *entrance*. Third, those which have a relatively uniform movement along the entire face of the jaw.

Construction of Jaw Crushers.—The jaw crusher was invented by Ely Whitney Blake in 1858 and was first used for crushing rock for road work. With the exception of the point at which the movable jaw is pivoted the construction of all jaw crushers is similar. Figures 61 and 62 show views of typical jaw crushers.

In the crusher shown in Fig. 61, the reciprocating motion is given to the jaw by means of an elliptical cam. As the shaft revolves, a backward and forward motion is given to a rocker arm which in turn communicates this motion to the jaw through a small breaker bar. This breaker bar is the weakest part of the crusher and protects the rest of the machine from breakage in case unexpected hard material, such as iron, falls in between the jaws.

Another common method of imparting a reciprocating motion to the movable jaw is by means of an eccentric and toggle joint. In this case a so-called "pitman" is mounted eccentrically on the rotating shaft, thus receiving a motion upwards and downwards in the vertical direction. The lower end of this pitman is connected to a toggle joint, one arm of the toggle being fixed to the rear frame of the crusher and the other arm being fixed to the movable jaw. This construction, being more powerful, is used on the large jaw crushers, particularly of the Blake type.

Jaw Crusher Control.—The size of the crushed material is governed in two ways, first, by changing the distance between the jaws at the point of discharge, and second, by the length of stroke of the movable jaw. The distance between the jaws may be regulated by means of wedges so that the fixed jaw is moved forwards or backwards, thus decreasing or increasing the discharge opening. The length of stroke may be changed only with difficulty.

Blake Type of Jaw Crusher.—In the Blake crusher, Fig. 61, the material to be crushed enters the jaw at the top, is crushed by

continuous pressure, and by its own weight falls toward the bottom. As it falls, it is successively crushed finer and finer, and drops from between the jaws at the bottom. On account of the fact that the greatest motion occurs at the point of egress, the Blake type of crusher eliminates the danger of choking and may, therefore, be used in the crushing of material which has a slight tendency to pack, and this type of crusher can handle without difficulty most material containing 5 to 10 per cent of water. On account of the great range of motion between the jaws at the point of discharge, the Blake crusher delivers a product which is uneven in size, *i.e.*, there is considerable variation

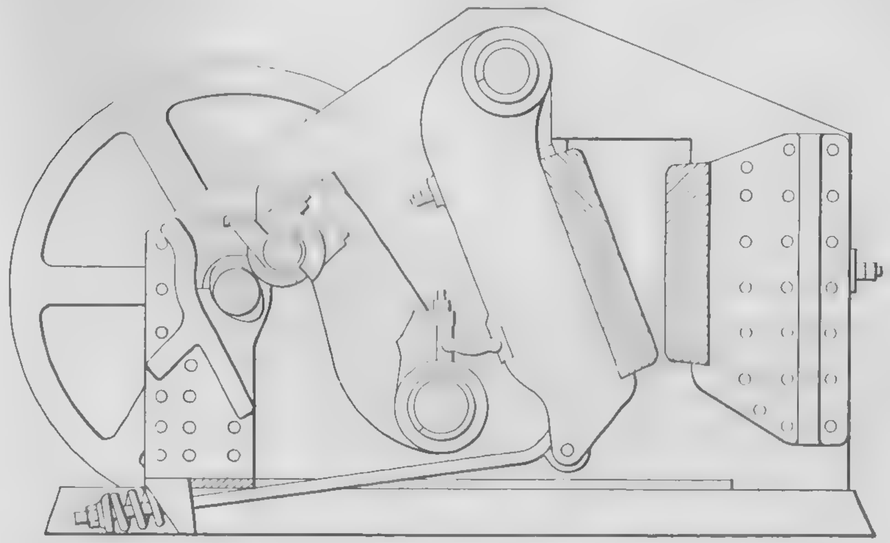


FIG. 61.—Jaw Crusher, Blake Type.

between the large and the small lumps discharged from the machine. In view of the fact that a jaw crusher very rarely delivers a finished product, this disadvantage is not serious.

The main wearing parts of jaw crushers are the crushing faces of the jaws which are usually made of chrome (or manganese) steel or chilled iron and are so arranged as to be easily replaceable. Furthermore, the greatest wear is at the point of discharge of the jaws and the position of these plates may be reversed end for end, so that the top which is worn but little is placed at the bottom of the jaw. In this way the life of the plates may be considerably prolonged.

The advantages of the Blake type of jaw crusher lie in its large capacity, the low cost for repairs, low power consumption per unit of product and its freedom from choking. It has the disadvantage that the size of the product is quite variable and also the minor drawback that its action is intermittent instead of continuous, that is to say, crushing occurs only on the forward stroke of the jaw.

Dodge Type of Jaw Crusher.—In this crusher the movable jaw is pivoted at the bottom. (See Fig. 62.) Since the minimum movement of the face is at the point of egress of the stock, this

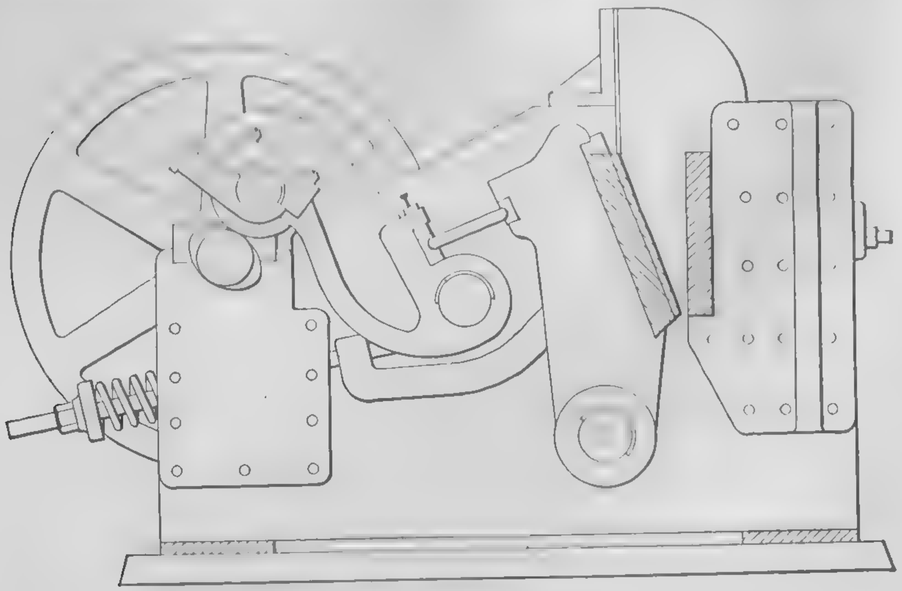


FIG. 62.—Jaw Crusher, Dodge Type.

crusher gives a more uniform product than the Blake but does not clear itself when choked. In consequence it can be employed only for free-running material.

Roll Jaw Crusher.—In the roll jaw crusher the face of the movable jaw is so shaped and the motion imparted is such that the face of the movable jaw rolls along the face of the fixed jaw plate. The movable jaw of this type of crusher is pivoted at the top, and the motion to the movable jaw is imparted at a point in between the top and bottom of the jaw and from a movable pivot situated well back from the discharge opening. The roll jaw crusher is a compromise between the Blake and the Dodge types

of jaw crushers and as such it does not possess so prominently the advantages or the disadvantages of these machines. Thus, while they are not so liable to clog as the Dodge they deliver more uniform product than does the Blake. However, they do not have the capacity and low power cost of the Blake nor the uniformity of the Dodge. Furthermore they are more complicated in construction and the field of their use is limited.

Gyratory Crusher, Gates Type.—A sectional elevation of the Gates gyratory crusher is given in Fig. 63. The breaker crushes by rotating eccentrically a truncated conical head, 7, which has its

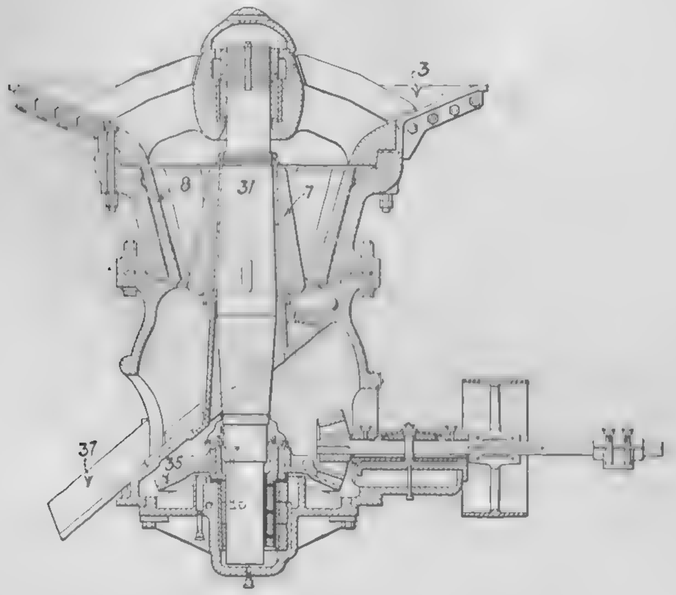


FIG. 63.—Gyratory Crusher, Gates Type.

small end up, inside of a truncated conical ring 8, which has its small end down. The truncated cone is mounted on a shaft 31, which is pivoted at the top in a semi-universal joint. The lower end of the shaft is mounted eccentrically in the gear 35, so that as this gear rotates, the shaft receives not only a rotary motion but also a gyratory motion thus causing the inner inverted truncated cone to alternately advance toward and recede from any given point on the truncated ring. It is further to be noticed that the greatest relative motion between the inner cone and the

outer ring is at the lower end or the point of discharge, thus giving to this machine many of the advantages of the Blake type of crusher. Also, this machine is continuous in its action, and, the motion being rotary instead of reciprocating, the vibration is reduced to a minimum.

The material to be crushed is fed in through the hopper 3, and is crushed between the inner cone and outer ring by continuous pressure through the successive advances of the inner cone, and is discharged through the spout 37. The size of the particles being discharged from this machine is regulated by raising or lowering the shaft 31 to which the inverted truncated cone is fastened. This produces a smaller or larger opening in between the cone and the ring, but such regulation is quite difficult compared to the easy control of a Blake jaw crusher.

The Gates gyratory crusher will handle pieces of rock from 6 to 60 in. in diameter and will reduce them to pieces of $\frac{1}{4}$ to 4 in. in diameter. An advantage of the gyratory crusher is that it has a relatively large feed opening compared to a small discharge opening, and, therefore, the range of reduction in one pass through the machine is large. A gyratory crusher with a large feed opening has an extremely large capacity, consequently, these machines should be used only when such capacity can be utilized. In other words, if a small amount of very large pieces of rock are to be crushed, the Blake type of jaw crusher is more suitable than the gyratory crusher, owing to lower initial cost. However, if a large amount of large size rock is to be crushed then the gyratory crusher is the more suitable machine, because the power per ton of material is lower than in the case of jaw crushers. The original installation cost and the maintenance cost of gyratory crusher is greater than that of the Blake jaw crusher so that the selection of a preliminary crusher involves balancing the costs of initial investment, maintenance, labor and power. The gyratory crusher also possesses the advantage of being able to handle material directly from the bin without a feeding attachment, and can therefore form the bottom hopper of a storage bin, taking the feed directly from such bin without clogging.

II. INTERMEDIATE CRUSHERS

As mentioned previously, there is considerable overlapping in the fields occupied by various crushers, and different machines will occupy different fields depending upon the kind of material to be treated. A type of machine which may be said to occupy this intermediate field is the Symonds Disk Crusher, although crushing rolls, which will be taken up under fine crushers, might also come under this classification.

Symonds Disk Crusher.—In the types of crushers previously considered the only force tending to remove the material is the

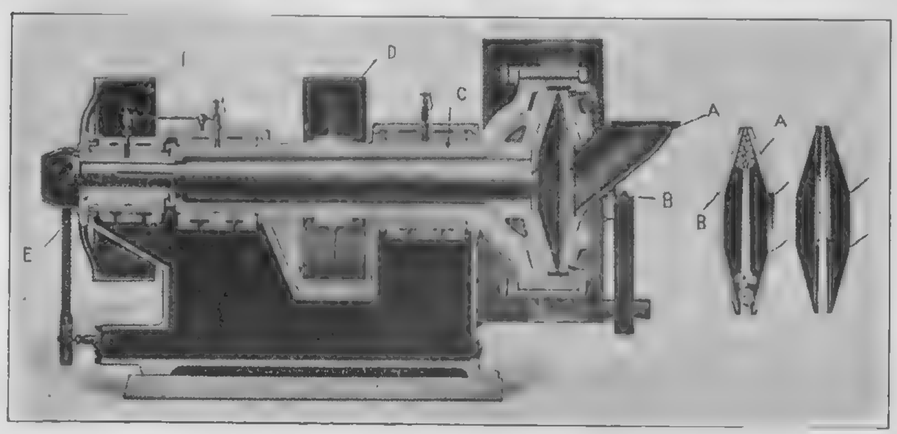


FIG. 64.—Symonds Disk Crusher.

force of gravity. If the material being reduced is damp or of a sticky nature, there is a liability to clog especially with the gyratory. A new principle is introduced in the Symonds Disk Crusher (Fig. 64) in that centrifugal force throws the pieces out of the crushing zone as soon as they are small enough to escape through the opening between the faces. The crushing force is applied by two saucer-shaped disks, *A* and *B*, which rotate in the *same* direction at the *same* speed. The outer disk, *A* (Fig. 64), is held in a bell-shaped cage fastened to the hollow shaft, *C*, driven by the flywheel, *D*. The inner disk, *B*, is supported by the ball-and-socket joint and solid shaft inside the hollow shaft, *C*. This solid shaft is driven by a flywheel, *F*. The rear end of the solid shaft is supported in an eccentric bearing, *E*, which causes

the disk, B, to be always at an angle to the shaft, C, and disk, A. When the material to be crushed is introduced between the disks, it is thrown to the outside and caught by the disks at the point of widest opening. It is carried around by the disks which rotate together and as the rims of the disks now approach each other due to the eccentricity of their two shafts, crushing action is exerted and the material is broken by direct, continuous pressure. This action is independent of any rotation of the eccentric bearing E, which is set in the head of the pulley F, and the crushing action would take place even if the latter were at rest; but by rotating the hub through the pulley, F, the advance and retreat of the two disks are multiplied at each revolution and the crushing capacity increased. The crushing strain is taken up by the large ball-and-socket joint in the head of the machine.

The size of the product may be varied and the wear and tear taken up by changing the distance between the crushing disks. This is accomplished by removing the segment plates behind the disks and replacing them with others of the desired thickness. Owing to the promptness with which the crushed material is ejected from between the disks, the product is uniform and the capacity relatively great.

The Symonds disk crusher can break material down to $\frac{3}{8}$ in. in diameter. The feed for these machines should not be over 6 in. in diameter and then they are capable of handling from 5 to 100 tons per hour, depending on the size of machine, size of feed and fineness desired.

III. FINE CRUSHERS

Crushing Rolls.—In the gyratory crusher, the crushing head was made to roll upon the inner surface of the conical ring while traveling on the circle within it, and for coarse crushing this principle works satisfactorily; but for fine crushing such application of the roll principle would be impracticable owing to the lack of constancy of the distances between the two crushing surfaces. However, the rolling principle is utilized by providing two cylinders mounted upon horizontal shafts which revolve towards each other. The rotating surfaces nip the lump of material and gradually draw it in between them and crush it to a size determined by the distance separating the faces at their nearest point.

A typical machine is shown in cross-section in Fig. 65. The diameter of the crushing rolls is greater than the width, and while both dimensions vary considerably from machine to machine, these rolls average 14 in. in width and 36 in. in diameter. They consist of a central permanent core of soft iron forced upon movable shafts and are fitted with a replaceable wearing surface of hardened steel. They are maintained a constant distance apart by blocks and are held in place by powerful springs which give way when non-crushable material is accidentally introduced. These springs retreat slightly as the regular product passes through the rolls, so that in general the ratio between the size of opening and the size of product is 0.8, that is, rolls which have a $\frac{1}{2}$-in. opening will produce a material that is $\frac{5}{8}$ in. and

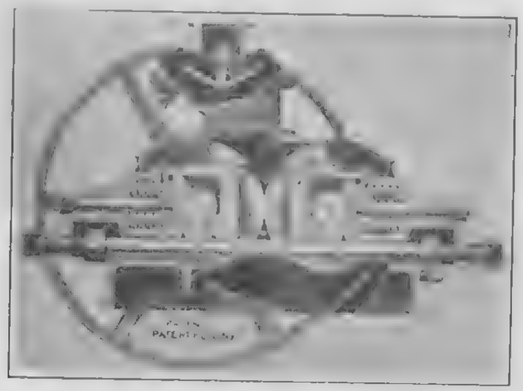


FIG. 65.—Sturtevant Crushing Rolls.

under. It is vital to have an even distribution of feed across the faces of the rolls, otherwise they will groove and deliver a product containing much oversize material. This not only causes unsatisfactory operation of the rolls, but also increases maintenance, decreases the volume of output and increases the power consumed. Therefore, such crushing rolls should be fed with an automatic device which will spread the material uniformly along the faces.

In the machine shown in Fig. 65, the material being crushed is fed through the automatic reciprocating feeder, of a satisfactory type, falls between the faces of the two crushing rolls and is gradually drawn in between them. The angle, made by the tangents at the point where the largest piece the roll will "bite" meets the roll faces, is called "Maximum Angle of Nip," and for

most materials is about 50°. The relation between the size of feed, space between the rolls, the radius of the rolls, and the angle of nip is given by the formula

$$\frac{r+a}{r+b} = \text{cosine } \frac{N}{2},$$

where

r = radius of the rolls;
a = ½ space between the rolls;
b = radius of the particles to be crushed, and
N = angle of nip, in degrees.

Crushing rolls are advantageously used when the material is brittle and if crushing is desired with a minimum of dust. Materials fed to such rolls rarely exceed 1½ in. and for the minimum power consumption and the maximum production, the ratio of reduction in size per pass should not be greater than 4 : 1. Crushing rolls may be used for grinding material down to a fineness of 10 to 15-mesh, and in some cases a little finer, but in general it is more satisfactory to use ball mills when the size desired is finer than 10-mesh (Tyler standard screen). If the material is not to be ground below 10 or 15-mesh there are no better machines made for the work, and on account of their relatively large capacity and freedom from dust, together with their simple construction, such rolls are used extensively. Wet materials may, if desired, be crushed to 20-mesh.

As mentioned above, the size of the material discharged from the crushing rolls is determined by the distance between their faces at the nearest point. Therefore, in selecting crushing rolls it is highly desirable to be able to adjust easily the opening between the rolls to the proper distance, especially when a minimum of fines or dust is desired, because easy adjustment facilitates maintenance of good operation. Arrangements should also be provided so that the rolls may be set up more closely as wear takes place. Some rolls are adjusted by means of shims placed between the journal boxes of the rolls and fixed supports on the crusher frame. In other makes, the distance between the roll faces is adjusted by worm gears moving the journal boxes backwards or forwards. This latter method is simple and capable of quicker control.

The strong points of crushing rolls are simplicity and ruggedness, and the small amount of fines or dust produced when operated under proper conditions, namely, an even feed and the ratio of reduction not over 4 : 1. They are unsurpassed in producing a coarse granular product, and they show up to disadvantage only when used in fields for which they are not suited, such, for example, as producing fine material by means of choke feeding.

There are many special designs of crushing rolls for handling special products. For example, one type crushes the material against a fixed plate by a single roll whose rotating face is studded.

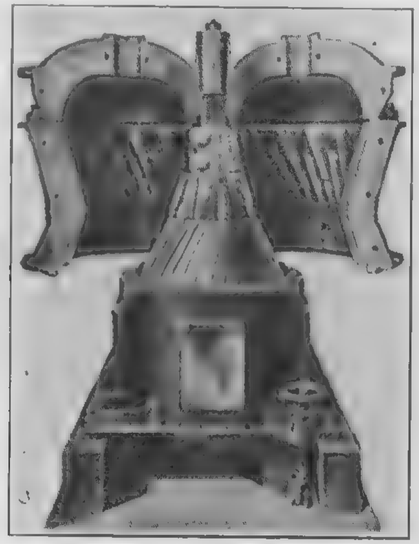


FIG. 66.—Sturtevant Rotary Crusher.

Such a crusher is used for material containing cleavage planes, such as coal, etc.

Rotary Crushers.—The rotary crusher is a special type of machine suitable for handling soft, friable material, such as coal, coke, tan bark, etc., if the material fed to the crusher is not over 3 to 6 in. in size. Under such conditions the rotary crusher will produce a product whose diameter is ¼ to ¾ in. in length and under. Such crushers are sometimes known as "Coffee Mills."

In Fig. 66, it is seen that the crushing action takes place between an inner rotating grooved cone and an outer grooved ring.

The adjustment of this machine to produce finer or coarser material is by means of a small hand wheel (shown in the lower right-hand corner) which raises or lowers the step-bearing on which the rotating grooved cone is mounted.

This machine has a relatively large output and low maintenance when used on suitable material, and delivers a fairly uniform product. However, only comparatively few materials can be handled, and consequently this mill does not have a wide use.

Stamps.—Gravity stamps or mills, may be used to crush material from a maximum diameter of $1\frac{1}{2}$ in. down to a minimum diameter of 40-mesh (Tyler standard). The material to be crushed is fed into boxes or mortars and subdivided by blows from stamps or hammers weighing about 1000 pounds. These hammers are raised by means of cams and are allowed to fall on the material to be crushed, thereby reducing it by blow or impact. Stamps are largely used in wet crushing (water 50 per cent or over) but their present day field is almost wholly confined to the gold mining industry where crushing and grinding takes place simultaneously with cyaniding or amalgamation.

The fineness to which the material is ground is regulated by the size of screen which surrounds the mortar boxes, by the weight of the stamps, and by the rate of feed of water and ore.

Outside of the field mentioned above, stamps are not used on account of their high power cost and large initial cost per ton of output. It is obvious that the power required is not proportional to the work done, since the power consumption stays constant whether there is any material in the mortar boxes or not. Furthermore, stamps produce more fines or dust than is usually desired.

Chilean Mill (Pan Rolls).—All the machines so far considered crush by means of a compressive force. It is possible to utilize also a shearing force and produce the action familiar to us when a nut is crushed by stepping on it and turning around at the same time. This is in principle a grinding and crushing force combined and has been utilized for many years in the machine known as the Chilean mill, Edge Runner or Chaser. It consists of one or more heavy steel rolls (formerly of stone) fixed on a horizontal shaft, and caused to rotate over a bed or track. Since the outside of the roll must travel over a greater distance than

the inside, there is a constant slip or shear. The feed is continually carried under the rolls by the plows, and when the operation is finished the product may be discharged by dropping a plate supporting a grid in the roll track. These machines are used when tough or plastic masses, such as clay for ceramics and black gunpowder, must be ground or mixed. Formerly they were largely used in the mining field, but here they have been replaced quite generally by ball mills.

IV. FINE PULVERIZERS

Ball Mills.—In all the mechanisms so far considered the crushing elements have been mechanically guided and the feed introduced between the moving parts. It is possible, however, to effect crushing by allowing flint rocks or pebbles, or balls of chrome or manganese steel to fall and revolve upon each other when held in a large rotating drum or steel-lined cylinder containing the material to be ground. This constitutes the Ball Mill, which has become popular on account of its simplicity of construction, ease of operation, absence of delicate parts, and low cost of maintenance. Ball mills are usually short in length and relatively large in diameter. They are generally supported and rotated on hollow axial trunions, through which the material is fed to the cylinder and from which the finished product is discharged. Fig. 67 shows the standard mill, while Fig. 68 shows a Hardinge conical ball mill. A standard mill is characterized by the fact that it is very short in comparison with its diameter. For example, in the largest size mill of this make, the diameter is approximately $10\frac{1}{2}$ ft., whereas the working length is only 6 ft. This mill is generally used in wet grinding and the entire discharge end is fitted with a grate. Between this grate and the end of the mill, there are lifters which elevate the product so that it will be discharged through the trunnion of the mill. For example, pulp or material to be ground is mixed with water and put in through a hollow trunnion on the feed side of the mill (right-hand side of the mill shown in Fig. 67) and flows across and down through the body of the mill in which the balls are tumbling, and then passes out through the discharge grating. Here the wet pulp is elevated by the lifters, and is ejected through the trunnion on the discharge side of the mill. There is a difference in elevation between the

feed as it enters the mill and the point of discharge through the grate. This causes the water to have a sluicing action which carries the fine material through the grate and out through the trunnion at the discharge end of the mill. This relieves the mill of the mass of pulp and causes the fines to migrate faster than the coarse particles. Tests seem to show that this difference in head through the mill gives better operation than the so-called "overflow" types of mill, where the material to be ground flows in the feed trunnion, through a cylindrical mill and directly out through the discharge trunnion.

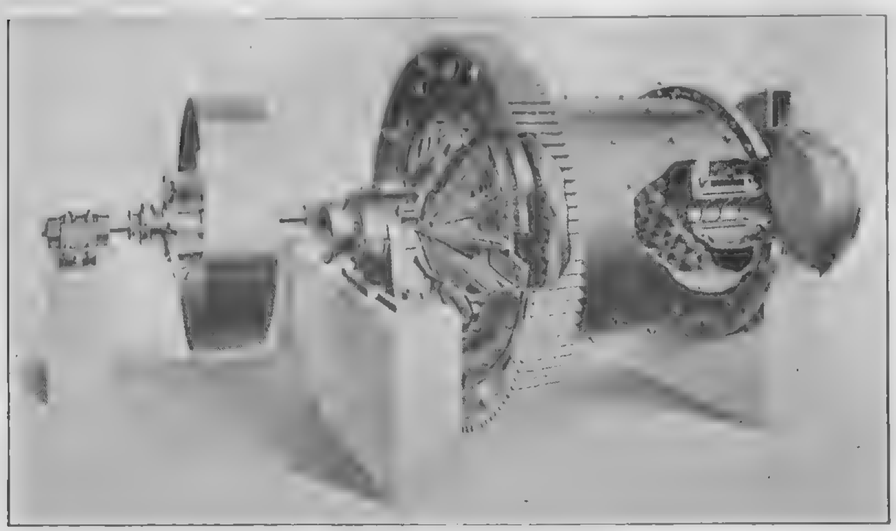


FIG. 67.—Allis-Chalmers Ball Mill.

The balls are introduced full-size, and wear away gradually, finally disappearing in the product, new ones being added from time to time to keep up the proper number in the mill. Therefore, after a mill has been in operation for some time, there will be found in it an assortment of sizes of balls, from freshly added ones down. New balls must be large enough to crush the largest particles in the feed, but are too large to handle the fine particles of the product efficiently. This, together with the cushioning action of the fines upon the coarser particles, causes waste of power.

The unique feature of the Hardinge Conical Ball Mill, shown in Fig. 68, is the action brought about by the shape of the rotating

shell in classifying the crushing balls. This classifying action causes the larger balls to assume a position at the large diameter of the mill. Towards the discharge end of the mill, its diameter gets smaller and at these smaller diameters will be found the smaller or worn balls. The same action takes place in connection with the material to be ground. The material, fed in through a scoop at the feed end of the mill (left side of mill shown in Fig. 68), remains in the large diameter of the mill until first crushed. As its subdivision proceeds, it gradually works its way along the cone, and is finally discharged in a finely ground condition through the trunnion at the opposite end of the mill. In this way the

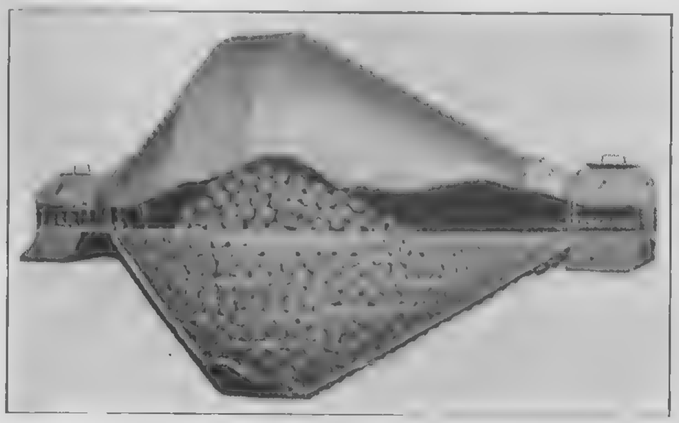


FIG. 68.—Hardinge Conical Ball Mill.

large pieces of material to be ground are broken up by the large balls, and the small pieces by the small balls, with the result that the power consumption is decreased. The discharge end of the Hardinge mill is usually about 2 or $2\frac{1}{2}$ in. lower than the feed end.

Ball mills will handle a feed containing lumps as large as $1\frac{1}{2}$ to 2 in. in diameter and may be used to produce material practically all of which will pass a 50- or 60-mesh standard screen. These mills may be used for wet grinding, in which case the moisture content is usually 50 per cent or greater. Even when grinding abrasive material the ball consumption does not amount to over 0.7 lb. of iron per ton of material ground. However, for most materials, the ball consumption will not amount to one-half this figure providing the mill is fed with sufficient material to prevent one ball from falling or pounding on another. The

material being ground should always cushion the fall of these balls as they rotate in the mill, and the sound coming from the mill should be a dull rumble, indicating an absence of metal to metal contact.

In the case of ball mills, the crushing action is by impact or blow of one ball falling upon another ball with the material in between. There is a certain amount of grinding or shearing action taking place in the mill, due to rolling of the balls, but its importance is small compared to the action of the falling balls.

The fineness of the discharged product from a ball mill may be governed by the following methods:

1. *By Changing the Rate of Feed.*—Increasing the rate of feed in a ball mill decreases the fineness, since the material remains in the mill a shorter time, being crowded out by the incoming feed.

2. *By Changing the Diameter of Feed.*—It is obvious that increasing the diameter of the particles fed to a ball mill will decrease the fineness of the discharged material if the *rate* of feed is maintained constant.

3. *By Increasing the Total Weight of Balls.*—Increasing the total weight of balls of a given size increases the fineness of the discharged product, providing the rate of feed is kept constant. This increase in weight of balls may be brought about either by adding additional balls to the mill up to the capacity which can be handled (roughly 50 per cent of the cubic contents of the mill) or by increasing the specific gravity of the balls. For example, either the capacity, or the fineness of the discharged product, may be increased by changing from flint to iron balls as grinding media.

4. *By Changing the Diameter of the Balls.*—Large balls tend to produce a coarse, granular product, whereas small balls produce a finer pulverized product. Ball sizes usually run from $\frac{3}{4}$ in. in diameter to 5 or 6 in. in diameter, and for coarse crushing an assortment of 3-, 4- and 5-in. balls, would probably be used whereas for fine crushing an assortment of $\frac{3}{4}$- to $1\frac{1}{2}$- or 2-in. balls would be preferable.

5. *By Changing the Slope of the Mill.*—Increasing the slope of the mill or lowering the discharge opening decreases the fineness of the product. Such a procedure also increases the capacity of the mill.

6. *By Increasing the Freedom of Discharge.*—In ball mills having the discharge grating, the fineness of the material may be

decreased by increasing the size and number of openings in the discharge grating or plate. This also increases the capacity of the mill.

From the standpoint of tonnage, ball mills may be used for as small an output as two or three hundred pounds per hour up to a production of fifteen or more tons per hour.

Maintenance of a ball mill is extremely low, inasmuch as there are only two or three bearings and these are so located that they may be enclosed in dust-proof journals. Furthermore, the mill is a low-speed machine, usually operating at from 22 to 30 r.p.m. Practically all of the wear and tear occurs in the liners of the mill and the balls and liners must be replaced at infrequent intervals, depending largely upon the tonnage and abrasiveness of material ground. Most of the wear inside the mill occurs on the balls, and additional balls are thrown in the mill, either daily, weekly, or at other intervals, depending upon the tonnage ground. This extremely low maintenance is one reason for their popularity. Furthermore, they are simple to operate, and cost of installation and power consumption is extremely low. The product is not, however, at all uniform in size, and as previously mentioned, rolls are more satisfactory if the product is to be coarser than 8- or 10-mesh. Also, rolls are better, if the material is moist, because ball mills can handle only material either relatively dry (under 3 or 4 per cent water), or else very wet (over 50 per cent water), as moist material packs around the balls and cushions them.

When the production of extreme fines is objectionable and the grinding is done wet, efficient work is accomplished by passing the charge through the mill with relative rapidity, and immediately into some sort of a hydraulic classifier. The overflow is taken off as finished product, while the oversize is returned to the mill, or is fed to a second mill with smaller balls. This is known as closed circuit grinding, and when circumstances permit it, is to be recommended.

Mills of the Marcy and Hardinge type will grind ore from a gyratory or disk crusher so that only 2 per cent will be on a 48-mesh screen and 60 per cent will pass a 200-mesh screen with a power consumption of only 10 to 12 k.w. hours per ton.

Tube Mills.—There is relatively little difference between tube mills and ball mills. In general, a tube mill, Fig. 69, may be considered as an elongated ball mill, that is to say, a mill that is

relatively long in comparison with the diameter, in contrast to a ball mill which is relatively short in comparison with the diameter. The construction, the method of adjustment and control is the same as for ball mills. The difference between the two machines lies in their different spheres of usefulness, the ball mill being suited to fine crushing, granulating and comparatively coarse pulverizing (so that 95 to 98 per cent passes through 50- or 60-mesh) whereas tube mills are used for still finer pulverizing. The tube mill is important in the cement industry where a large quantity of material must be ground to a fine state of subdivision in equipment that is as simple as possible in design. Tube mills vary in size from 10 to 30 ft. in length, and from 3 to 8 ft. in

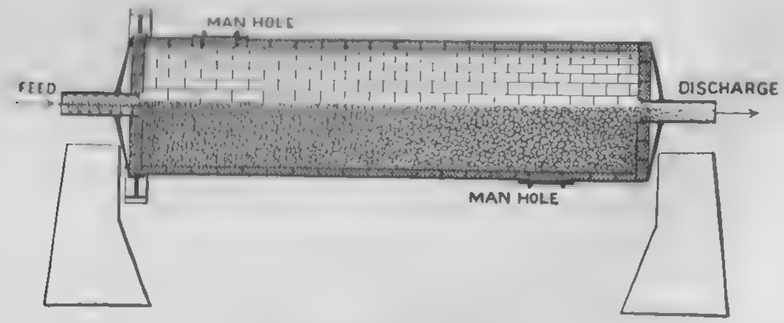


FIG. 69.—Tube Mill.

diameter. A 5-ft. by 26-ft. mill will grind from 75 to 95 tons of medium hard material from 20-mesh to 150-mesh per 24 hrs.

Centrifugal Roll Mills.—The principle of rolling one element upon another has been widely used at all times in the design of crushing and grinding machinery. It has been seen that the gyratory crusher uses it to some extent, while crushing rolls and the Chilean mill are based wholly upon this principle. There are a number of other mills that use the same principle in a modified form, by developing the pressure between one element and the other by the use of centrifugal force. Most of these mills have been designed to meet the necessity that has arisen in certain specific fields, and they are difficult of classification from the standpoint of the size of product handled on account of serious overlapping. In general they crush the material not only by direct pressure but they also grind by attrition (shear). The Huntington,

Griffin, Bradley, Maxecon, Sturtevant ring-roll, Fuller-Lehigh and Raymond mills are all of this class.

Sturtevant Ring Roll.—As mentioned previously, when material is to be finely crushed or pulverized, small rolls, set close together are not economical. To meet this situation, rolls have been

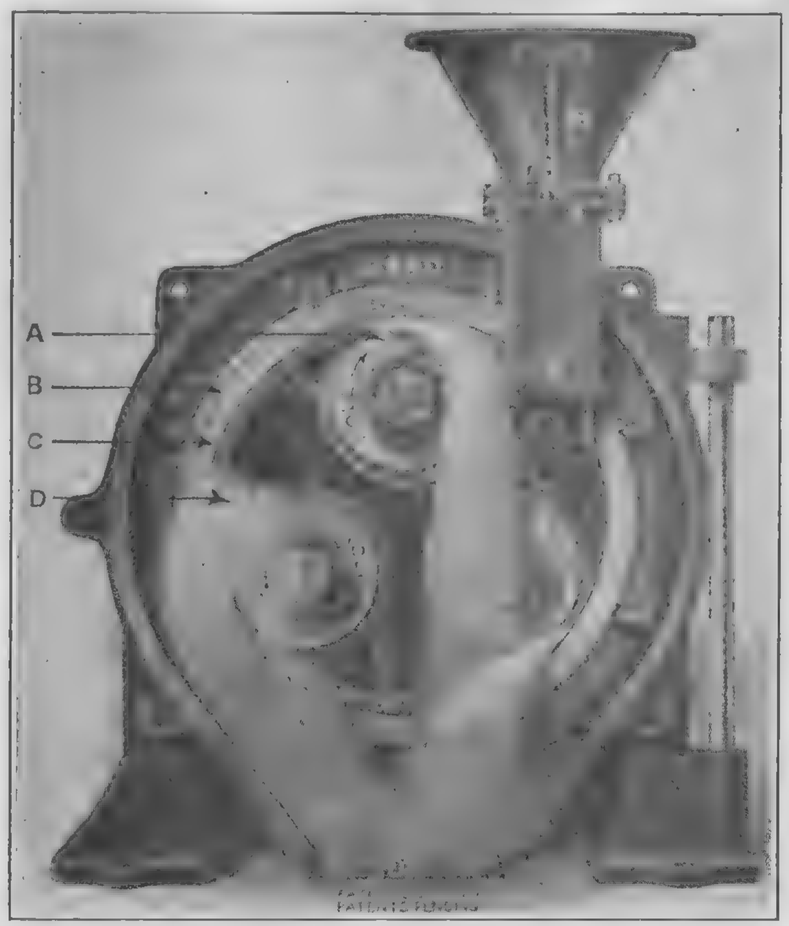


FIG. 70.—Sturtevant Ring-roll Mill.

designed which travel rapidly around the interior surface of a ring in a manner somewhat similar to the gyratory crusher, or conversely, the rolls may be in a fixed position, and the outer crushing surface rotated. The only machine of this latter type is the Sturtevant ring-roll, shown in Fig. 70. The ring, *B*, having a concave inner face is rotated at a relatively high speed, and

material to be crushed is fed into the hopper, H, through the spout, S, between the ring and one of the rolls, A. This roll has a convex surface and is pressed up against the outer ring by powerful springs, acting through an elbow joint. The material is crushed as it passes between the roll and the ring, and some of the finer material is thrown off through the discharge. Centrifugal force holds a large amount of the material, C on the ring which passes underneath the next roll. In this way, the material is carried around and around under successive rolls, until it finally works its way out of the mill, being crowded out by incoming feed. Oversize material is screened in an outside separating machine and returned to the mill for further grinding.

Fuller-Lehigh Mill.—The Fuller-Lehigh mill may be designated as a centrifugal roll mill in which the roll is replaced by balls held in sockets. It has a number of heavy steel balls which are rolled at high speed around the inside surface of a grinding ring. The material to be ground is fed through a hopper to a screw conveyor at the top of the mill, is dumped into a center cage and then thrown against the ring by the motion of the balls and pushers. Attached to the rotating cage is a series of fan blades which elevate the finely crushed material and force it against the screen directly above the blades. Material that is sufficiently fine passes through the screen, whereas the material that is too coarse falls back into the crushing zone and is again thrown between the balls and rings. The fineness of material from this mill is largely governed by the rate of feed and the screen size. When properly adjusted it may be used for very fine grinding and is quite largely used for grinding coal for powdered coal burners, and in the grinding of cement.

Raymond Mill.—The Raymond roller mill shown in Fig. 71 has been successful very largely on account of the fact that the mechanical details are well-worked out, because it is a complete grinding unit and on account of the success of its air separator. The material is fed in through spout, S, Fig. 71, and is delivered to the mill at a uniform rate by the feeder, F. It is ground between the rollers, R, and the annular grinding ring, B. The rolls, R, are attached to a spider, which is rotated by a shaft driven from beneath by bevel gears, and centrifugal force causes the rolls to fly outward and crush the material against the stationary annular ring, B. These mills are made with two to five rolls, depending upon the capacity of mill desired. The material that falls from between the roll and the ring is picked up by plow, P, and again driven back into the sphere of crushing action. Air is led in through the passages, G, and picks up the finely ground material and carries it up through the slightly conical dome which encloses the rolls and their shafts. Here the velocity of the air

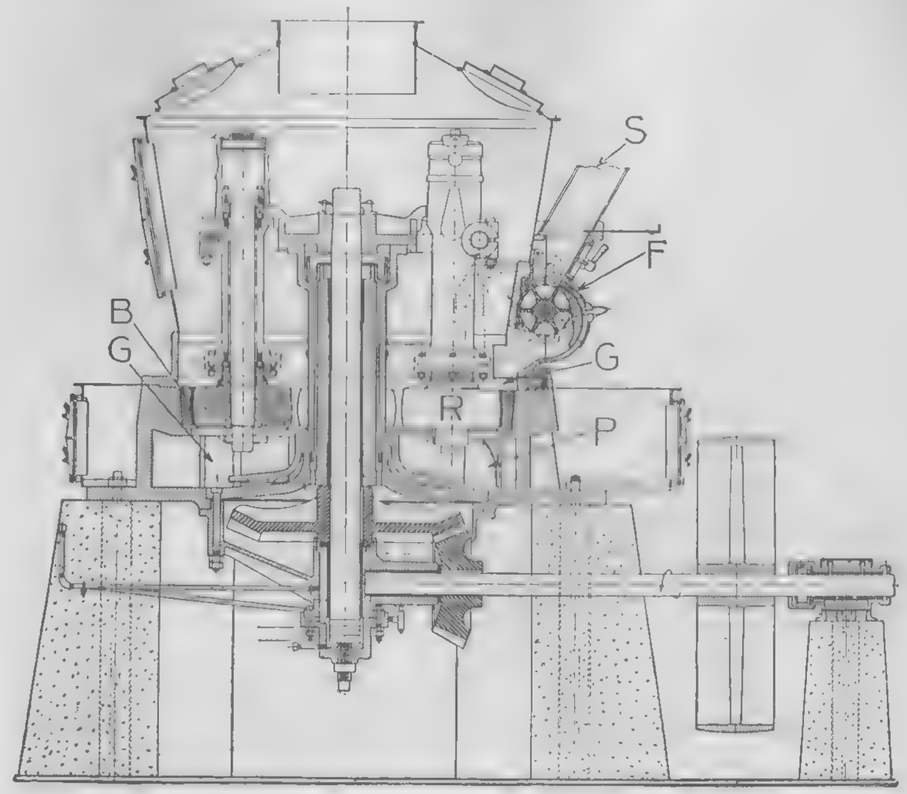


FIG. 71.*—Raymond Mill.

* See also page 318.

is somewhat decreased, allowing the coarser material to again drop back between the crushing rolls and the rings, while the fine material is carried up through a fan and tangentially into the top of a collector. The tangential motion, together with the decrease in velocity, due to the increase in cross-section, throws out the finely ground material which drops through a slide at the bottom of the collector. The air, thus freed of dust, is returned

to the base of the mill where it again picks up the finely ground material, and the cycle is repeated.

There are two types of Raymond roller mills, one known as the "Low Side" and the other, as the "High Side," the low side mill being the one just discussed. The high side mill differs from the low side mill in that it has a separator (Fig. 72), placed on the mill between the rolls and the fan. The air, laden with material that has been ground, passes between the inner and outer cones in this separator. At the top of these inverted, concentric cones, the air passes through gates set at the periphery of the base of the cones, and into the large inner cone. These gates may be set at varying angles so that the swirling, tangential

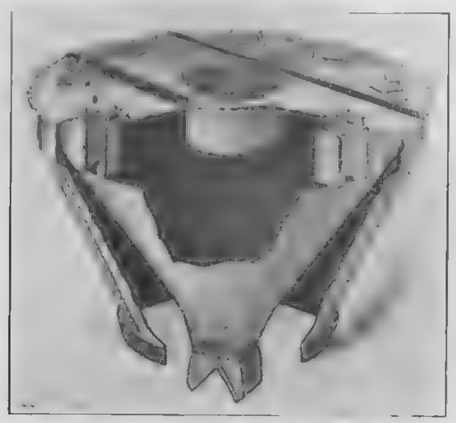


FIG. 72.—Raymond Separator.

motion imparted to the air may be varied at will. In this inner cone there is a separating action similar to that already described for the collector. The more tangentially the air is sent to the separator, the finer will be the product carried by the air to the collector. The coarse material settles to the bottom of this inner cone and is again fed to the mill through the two spouts at the bottom of the inner cone. The air, bearing only the finest material, is carried through the fan and over to a large collector where the finely ground material is settled out.

It is thus seen that the air in a Raymond Roller Mill is used over and over again. However, there is always a small amount of air which is unavoidably admitted with the feed, and this is withdrawn from the system through a small pipe leading from

the return air pipe. The dust in this excess air is removed by means of bag filters.

The feeder of the Raymond roller mill shown in Fig. 71, p. 301, consists of a hopper, under which passes a corrugated roll. The speed of this corrugated roll may be changed gradually over a wide range by a series of pawls operating ratchets. The operation of the mill is effectively controlled by regulation of this feed device and of the separator gates.

Being a high-speed machine this mill is not suited for grinding hard, abrasive material, but for many materials, such as lithopone, phosphate rock, barytes, limestone, etc., it is extremely well suited. It will not handle moist materials nor those that soften on heating. For example, asphalt or hard pitch cannot be ground in this mill *without* foregoing recirculation of the air and sending all of the air to the bag dust filters. It is one of the best fine grinding pulverizers made, and will handle material ranging from $\frac{1}{4}$ in. in diameter down to material that will all pass a 200-mesh screen. A five-roller mill, which requires 50 h.p. to drive the mill and 40 h.p. to operate the fan will produce about five tons per hour of material ground so that 90 per cent will pass a 200-mesh screen.

Unless the material being ground is abrasive, maintenance cost on these mills is low, although they are run at high speed and are used for fine grinding; furthermore, power cost is relatively low considering the range of fineness over which they operate.

Other Types.—There are a number of roller mills somewhat similar in operation to the Raymond, such as the Bradley, the Griffin, and the Huntington mills. The Griffin mill has only one swinging roll operating against the inner face of the crushing ring.

Burr Mills.—One of the oldest forms of grinding machines is the burstone mill, consisting of two flat stones, one rotating on the other. The center part of each of the flat faces is slightly dished, whereas the outer rim portion is flat. This outer rim is known as the "face," and it is on this face that the grinding is accomplished. In order to facilitate grinding action, radial grooves are cut from near the center axis of the stone to the outer edge, and from these, shallower grooves fan out across the face. The depth of these grooves is governed by the fineness desired. Material is fed down through a hole in the center of

the top stone and is carried outwards by centrifugal force and by the grooves. As it passes from the center to the outside edge the rubbing action of the stones wears the particles to be crushed by attrition. These mills find considerable use in the paint industry, where it is desired to grind to a very fine state of subdivision and combine at the same time a mixing or rubbing action. The fineness of the product from such mills is controlled by the rate of feed, the dressing of the faces (depth of groove, etc.), and by the distance between the two grinding stones. When abrasive material is to be handled in such mills, the burstones are replaced by rock emery. Such mills have a relatively low capacity and high power consumption per ton output.

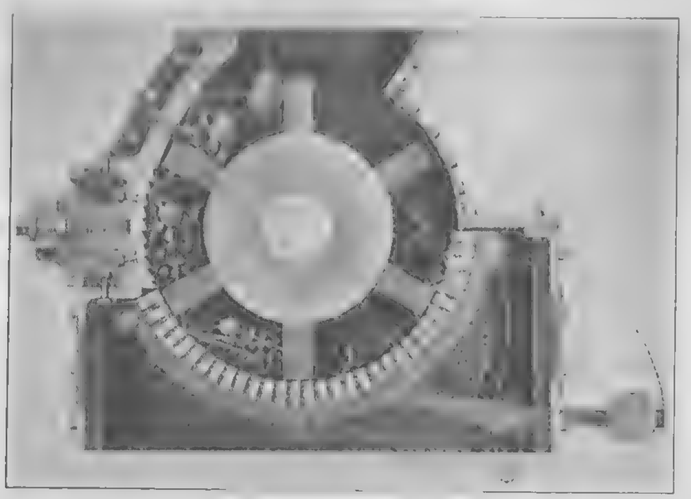


FIG. 73.—Jeffrey Hammer-bar Mill.

Disintegrators.—*Hammer Type.*—When it is necessary to crush material of a fibrous nature, or a brittle material which softens easily with heat, machines must be used which have a tearing action, or give a sudden blow, and these are usually called "Disintegrators." The principle involved in this type of machine is that of striking a blow while the material is suspended in air, as when a baseball is struck with a bat. The particle is hit with a force sufficient to crush or tear it, and yet with a velocity such that it does not adhere to the moving part. It is obvious that such mills will handle brittle as well as fibrous material. A mill of this type is the hammer-bar mill, shown in

Fig. 73. Hammers are flexibly fastened to an inner shaft or disk and the latter rotated at a high speed. Except when retarded by the material which is fed to the mill, these hammers, due to centrifugal force, extend radially from the center shaft. The material after it enters the beater box, remains there until pounded to a sufficiently fine state of subdivision so as to pass between the wedge-shaped grate bars covering the bottom of this box. Such mills may be used to crush wood chips, barks, and material of a fibrous nature, as well as shale, clay, bone, shells, etc.

Squirrel Cage Type.—Another mill of this type is the "squirrel-cage" disintegrator, consisting of "cages" built up of bars arranged in a circle, rotating at high speed. Often one such cage is placed concentrically between two others, the first rotating in the opposite direction from the other two. The material is fed into the center of the cages, is thrown out by centrifugal force, and is broken up by impact. These mills are excellent for material of not too great mechanical strength, which may be too damp and sticky to be handled in other types of apparatus.

GENERAL CONSIDERATIONS IN THE SELECTION AND LAYOUT OF EQUIPMENT

It is worth while to bring together the more important points which should be observed in the selection and layout of grinding equipment. These often prove helpful in reducing maintenance, in keeping production continuous and the quality of the product uniform. One must not, however, overlook those special local conditions which are often controlling in the treatment of the individual problem.

1. *Control.*—The apparatus should be so adjustable that the size of the product delivered can be changed easily over a reasonable range and so that, once the desired fineness is secured, the product will be delivered uniformly and continuously.

2. *Automatic Feed.*—The rate of feed is most easily kept uniform by having it automatic and this results in two advantages: First, it helps maintain uniformity in size of product and second, it keeps the mill running continuously at maximum capacity. The feeding device should be supplied from a large hopper or bin which acts as a reservoir to take up fluctuations in operation. It is usually advisable to have each unit in a series of machines equipped with individual feed and storage.

3. *Size Reduction by Steps.*—In laying out a department for crushing and grinding, it is best to operate in successive steps, without making the size reduction between the steps too great. As mentioned under "Crushing Rolls," reduction is most efficient when the ratio of reduction is not greater than 4 : 1, and wherever the tonnage to be crushed and ground warrants it, the ratio should be lower.

4. *Closed Circuit Operation and By-passing.*—The importance of these methods of operation must not be underestimated.

5. *Auxiliary Apparatus.*—It is always advisable to have the auxiliary apparatus, such as elevators, conveyors, screens, etc., oversize in capacity. In many crushing and grinding installations the output is not limited so much by the grinding mill itself as by some elevator, conveyor or screen. Oftentimes, in closed circuit grinding the amount of oversize material which has to be rehandled is underestimated in installing this auxiliary equipment. In general, when grinding in closed circuit, it is advisable to have such apparatus possess a capacity of about five times the output of the system.

CHAPTER X

MECHANICAL SEPARATION

PART I. SOLIDS FROM SOLIDS

The necessity for separating one solid from another may arise from a desire to accomplish either of two results: first, to sub-divide a mass of relatively homogeneous material existing in pieces or particles of different size, into fractions in each of which all individual particles are of approximately the same size; and second, to divide a mass composed of two or more individual substances into fractions so that each fraction will consist so far as possible of but one of the substances. It is seldom that both the above purposes can be attained in one operation.

Obviously, in order to effect a separation of any two materials of whatever sort, there must be found or produced in the individual units making up the mass, some inherent property in relation to which these individual units differ. The fundamental properties or conditions most commonly utilized in processes of separation are,

A. Dimensions of Units as affecting
1. Ability to pass through a given opening.
2. Friction manifested when falling through a resisting medium.

B. Density which may be either
1. True Specific Gravity.
2. Apparent Specific Gravity maintained for a short time.

C. Other properties.
1. Magnetism.
2. Electrical Conductivity.

A-1. SIEVES AND SCREENS

Introduction.—Separation according to the first sub-division is accomplished by giving the material opportunity either to pass through or be refused by an opening of definite dimensions. If the openings exceed $\frac{1}{3}$ in. in size they are generally expressed in terms of the linear dimensions of the largest particle which can pass through when the screen is in a horizontal position. When dealing with crushed rock for road building and concrete work it is common practice to describe the size of unit pieces as those which will pass through a ring of given diameter. When the openings are smaller than $\frac{1}{3}$ in. it has in the past been a general practice to speak of the size in terms of the number of such openings or meshes per linear inch. The latter is manifestly very inaccurate, for in a structure having any definite number of openings per linear inch, the actual size of the opening will depend upon the proportion of the inch which is taken up by the supports. Owing to the confusion which has existed in this matter for many years, the United States Bureau of Standards, in coöperation with certain enterprising users and makers of screens, has adopted as a basis for sieve construction a wire having a diameter of 0.0021 in. When woven into cloth having 200 openings per linear inch, the dimensions of each mesh produced is 0.0029 in. (0.0737 mm.). The ratio of the dimensions of the other sieves making a series is, of course, a matter of choice. A very rational basis for a screen scale is that proposed years ago by Rittinger, namely, that each opening shall be just twice that of the next smaller. The ratio of linear dimensions to produce this ratio of areas is, therefore $\sqrt{2}$, or 1.414. A very complete set of sieves has been produced in accordance with this plan by the W. S. Tyler Co., of Cleveland, Ohio. The size of the wire for the sieve cloth is so chosen that the ratio of opening above noted produces a relatively uniform series of sieves. When it is necessary to obtain a closer analysis for the finer sizes than is thus provided, it has been proposed to use for sieves having more than 65 meshes per inch a ratio of areas of $\sqrt[4]{2}$, or of linear dimensions of 1.189.

The separation of particles of different size by means of a screen or sieve is rendered difficult by two factors, both of which increase as the particles become smaller. The first of these is the *cohesion* of the individuals which tends both to carry very fine material along with the coarse, and to make a number of small units function as one large one, thus preventing separation. The second is the *adhesion* of the particles to the structure of the screening surface tending to make the openings smaller, or even stopping them altogether. An efficient screening system, therefore, provides, so far as possible, against the presence of these conditions. Since both cohesion and adhesion in a pulverized material are functions of the moisture content, it is apparent that to screen easily the mass must be either very dry or mixed with excess water. A further difficulty met with in very accurate separation is a tendency for the wires to spread, thus enlarging some openings, and closing others. This error is largely eliminated by proper screen construction and by using a secondary protective screen above the fine one to prevent the pounding effect of the larger pieces. It is obvious that the material to be screened must be kept in constant motion; only by giving the particles opportunity to take different paths can a separation be effected. Care must be exercised that in producing this motion the smaller particles be directed towards the openings through which they are to pass and not away from them. The violation of this principle renders some well-known types of apparatus for separation very inefficient.

Grizzly.—The simplest device for effecting separation is to provide a grating or perforated plate inclined at an angle greater than the angle of repose of the material to be separated. Across this surface the material is made to pass by the force of gravity, the smaller particles falling through, while the larger pass over. Such an apparatus may be easily made from heavy wedge-shaped iron bars held apart by distance blocks, and bolted together thus forming a frame generally known as a grizzly. By placing the small edge of the wedged-shaped bar downward, the narrow part of the slit is on top, and clogging is avoided. Such a frame is used in screening coal and crushed rock, and when made from heavy wire is employed for hand-separating sand and gravel. These types are to be recommended when accurate separation is not required, and when cheapness of construction and maintenance is a necessity. As will be explained later the angle at which a screen of this type is set is an important factor in determining the size of the particles passing through it.

When it is necessary to effect more perfect separation by such

an apparatus, the inclination of the screen is made less than the angle of repose, and the material to be screened is propelled along the surface by a motion imparted to the screen. This motion may be

a. Rotating.
b. Gyratory.
c. Reciprocating (bumping).

Rotating Screens.—In a rotating screen, frequently called a Trommel, Fig. 74,[1] the screening surface may consist of wire cloth, perforated metal, or iron bars and is formed into a long cylinder carried by an axial shaft and radiating arms, or frequently supported by circular rings running on friction rollers. The openings in the cylinder walls may be graded in size, or the

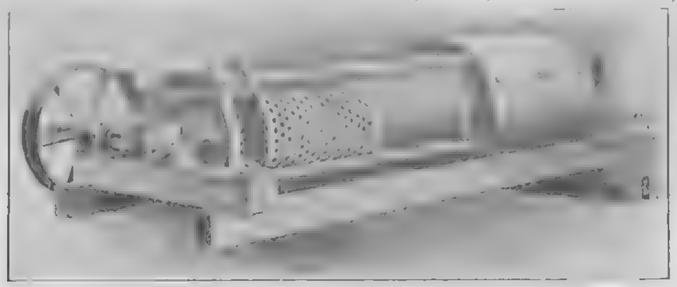


Fig. 74.—Rotary Screen.

cylinder may be made in sections, each section having openings of a definite size, so that the screened material may be drawn off in a number of fractions. The speed of rotation and the angle of inclination are so chosen that the material is carried uniformly forward from the feed to the exhaust end. The efficiency of such an apparatus is limited by a number of conditions. *First*, the large pieces at the entrance or fine end of the screen tend to spread the meshes and to drive the oversize through the small openings. *Second*, subjecting the fine screen to the impact of the heavy pieces greatly decreases its life. *Third*, the rotation of the charge tends to throw the larger pieces to the bottom of the layer; and this, it will be noted, is contrary to the relative position necessary for insuring the passage of the fine particles through the openings. *Fourth*, a very large percentage (90 per cent) of the area of the screen is not in action while the screen is in use. The first two objections are met by arranging a number of cyl-

[1] From Colo. Iron Works Co., Denver, Colo.

inders, each made of an increasing fineness, in series, so that the coarse screen comes first. The undersize of the first cylinder forms the feed for the second, while the oversize from the first is shunted off to its respective bin. Space may be economized by placing one screen within the others in a series of concentric drums. In this arrangement the coarse screen is at the center and each succeeding screen passes a finer material. If it be desired to operate the screens wet, or to wash the coarse material, as in the mining of phosphate rock, water may be introduced from orifices in the hollow shaft. In order to eliminate the end thrust on the bearings, rotating screens are frequently set with the axis horizontal, and the screening surface made conical or pyramidal instead of cylindrical.

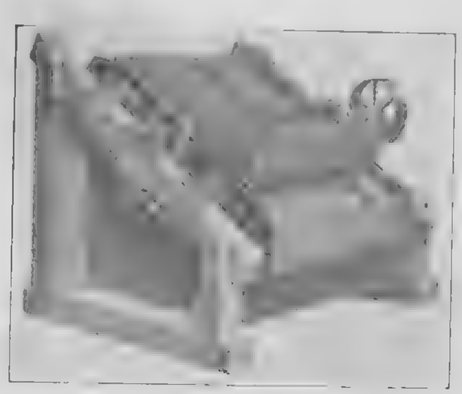


Fig. 75.—Impact Screen.

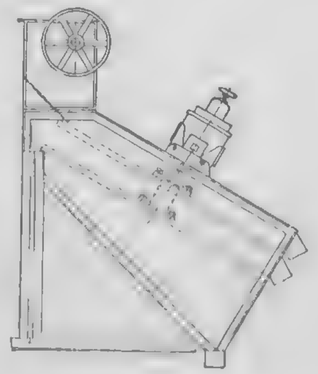


Fig. 75A.—Hummer Screen.

Vibrating Screens.—A large number of so-called shaking or vibrating screens, using both a reciprocating and a gyratory motion to keep the openings free and to propel the charge, are available, but it will be possible to mention but few of the types. The success of any vibrating screen depends upon maintaining clear, free openings. This may be obtained better by sharp rapid vibration than by any method of simply shaking the charge on the screening surface.

The impact screen of the Colorado Iron Works Co., Fig. 75, consists of a main frame on which is mounted the screening surface held in a vibrating frame of wood. This is flexibly supported by a pair of elliptical springs which force it upward against four adjustable cushioned stops. To this vibrating

frame, motion is imparted by two ratchets operating as multiple cams keyed to a revolving shaft. The effect of the cams is to force the vibrating frame with a sharp impact down against the springs, which, when the cams release the frame, carry it upward and outward. The meshes of the screen are thus kept free, and the charge is driven forward. The length of stroke, and inclination of frame are adjustable, and the apparatus as a whole may be easily adapted to wet screening. A motion at right angles to the face of the screening frame has a great advantage in that the heavier particles of the charge are thrown to the top, thus allowing the fine particles to come into immediate contact with the openings through which they are intended to pass.

In the Hummer electric screen of the W. S. Tyler Company, Fig. 75A, the wire cloth is given a positive and rapid vibration, by connecting it rigidly to an armature which is lifted by an electro-magnet, and repelled by a set of springs. The magnet is activated by a 15-cycle electric current supplied by a special generator furnished with this screen. The intensity of the vibration is regulated by adjusting the springs controlling the recoil of the armature. Rapid and efficient separation is thus effected.

In the Jeffrey vibrating screen made by the Jeffrey Mfg. Co., Columbus, Ohio, the screen frame as a whole is made to vibrate by a knocking motion, imparted to it by two eccentrics connected to suitable knocker blocks. The whole screen surface is given a motion of sufficient amplitude to maintain the meshes clean and to keep the charge moving toward the lower end of the screen.

As in other screens of this type the screen frame should be inclined at an angle of little less than the angle of repose of the material operated upon, in order that an undue proportion of fines may not be carried over with the tailings.

The Newaygo screen, Fig. 76, of the Sturtevant Mill Co. of Boston, Mass., is an inclined vibrating screen, built with a rigid steel frame on which the screen surface is held taut by a series of coiled springs. A sharp rapid vibration of the wire cloth is obtained by tapping the screen surface at a number of reinforced points with light hammer blows transmitted from the outside surface of the screen through wooden posts.

The design admits of either one, two or three screens, thus multiplying the number of products. It is in general found advisable

to provide a fine screening surface with a coarse protecting screen to carry the heavy particles present in the charge. This screen is called a "scalper" and greatly prolongs the life of the working screen by preventing both abrasion and the spreading of the meshes.

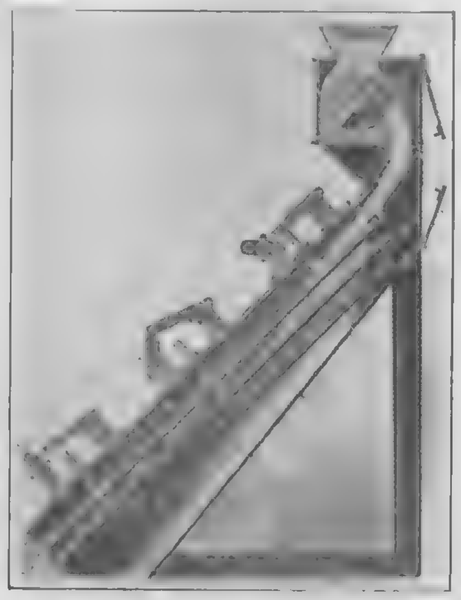


FIG. 76.—Newaygo Screen.

A-2. SEPARATION DEPENDING ON THE DIFFERENCE IN FRICTIONAL RESISTANCE OF PARTICLES WHICH VARY IN SIZE BUT NOT IN SPECIFIC GRAVITY

To make clear the principles which underly this method of separation, it is necessary to discuss the nature and governing laws of the forces which tend to oppose the motion of a solid body through a fluid.

Viscous Resistance.—When a solid body moves through a fluid so slowly that the latter flows past it in smooth stream lines, it is subject to a retarding force proportional to the relative velocity between the body and the fluid, and to the viscosity of the latter. For a small smooth sphere this retarding force can be shown [1] to be

$$F = 3\pi D\mu V,$$

[1] KIRCHHOFF, "Vorlesungen über Mathematische Physik," R. G. Teubner, Leipzig (1897).

where F is the retarding force, D the diameter of the particle, V its relative velocity, and μ the coefficient of viscosity of the liquid.

It will be noted that this "viscous resistance" is directly proportional to the first powers of the diameter and the velocity.

Eddy Resistance.—When, however, the velocity of the particle becomes large enough to set the fluid about it in eddying motion, the resistance due to the viscosity of the liquid, while still present to some degree, becomes negligible in comparison with another resistance, namely, the dynamic pressure set up by the fluid tending to oppose rapid motion through it. This "eddying resistance" is proportional to the square of the velocity, but it does not appear at all until a certain critical speed is reached. As a general rule it may be stated that a body moving in a liquid will assume that form of motion which at the existing velocity offers the *greater* resistance to its passage. The critical velocity is then the velocity at which the viscous resistance just equals the eddying resistance. For velocities in the immediate neighborhood of this point, neither set of laws holds, but above this transition range the laws of eddying resistance can safely be applied, and below it, those of viscous resistance.

For most substances in water this critical velocity is about 4 cm. per sec. corresponding to the rate of settling of particles less than 0.2 mm. in diameter. Such small particles constitute the slimes of metallurgical work, which are very difficult to separate by settling methods, partly because, as has been seen, they obey a different set of laws. The remainder of this discussion will therefore concern itself only with eddying resistance, which applies to the great majority of settling operations.

The calculation of this form of resistance is too complicated for a detailed treatment here. For a flat plane moving in a direction normal to its surface, the theoretical value can be shown[1] to be

$$F = 2Aw\frac{sV^2}{2g},$$

where A is the cross-sectional area, s the specific gravity of the fluid, and w the weight of a unit volume of water.

[1] LAMB, "Hydrodynamics of Fluids," 3d Ed., Cambridge Univ. Press (1906).

It is interesting to note that this is exactly the same as the force exerted on a fixed plane by a jet of water of cross-section A and velocity V.

In practice, due to water passing around the edges and exerting a compensating pressure on the back of the plane, the coefficient of velocity never reaches the theoretical value of 2, though values as high as 1.86 have been experimentally observed. For bodies approximately spherical in shape, the coefficient is found to vary from 0.44 to 0.58, the value 0.5 being a good average. Therefore, for spherical particles moving through a liquid,

$$F_f = \frac{(0.5)\left(\frac{\pi D^2}{4}\right)(62.3)(s)(V^2)}{2g} = 0.38D^2V^2s,$$

the units being pounds, seconds, and feet.

Consider now a solid particle in a fluid medium. If at any instant the force tending to move the particle exceeds the frictional resistance, the unbalanced part of this force will accelerate the particle (according to the law: unbalanced or resultant force = mass × acceleration) until it reaches a uniform velocity where the frictional resistance just balances the impelling force.

If, on the other hand, the frictional resistance be greater than the impelling force, the particle will be given a negative acceleration, or slowed down to a uniform velocity. In any case, then, a particle of given size and weight falling freely through a fluid quickly assumes a constant "free settling" velocity the magnitude of which is of great importance. It may readily be found by equating the frictional and other forces which are acting on the body, since these must be balanced to give uniform motion.

Gravity is, of course, the impelling force acting on a freely falling body. Using the previous notation, for a spherical particle,

$$F_g = \frac{\pi D^3 wS}{6},$$

where S is the specific gravity of the solid.

In any fluid medium, however, the solid body is buoyed up by a force equal to the weight of fluid displaced.

$$F_b = \frac{\pi D^3 ws}{6},$$

where s is the specific gravity of the fluid.

The resultant force, or "residual gravity" is then the difference of these two, or

$$F_r=\frac{\pi D^3 w(S-s)}{6}=32.6D^3(S-s).$$

Equating this to the frictional resistance gives for *spheres*,

$$F_r=F_f=32.6D^3(S-s)=0.38D^2V^2s.$$

Solving,

$$V=9.3\sqrt{\frac{D(S-s)}{s}}.$$

Or, for particles of *irregular* shape,

$$V=k\sqrt{\frac{D(S-s)}{s}},$$

where k is approximately 9.

The above derivation being perfectly general for any fluid medium, it follows that the same equation will hold for air as well as water; s being then negligible in comparison with S, one may write

$$V_a=k_1\sqrt{\frac{DS}{s}},$$

showing that the time necessary to fall a given distance becomes inversely proportional to $\sqrt{D}$.

Applications.—To make use of this property to separate a pulverized mass of particles into a number of different sizes, one may arrange a system like that shown in Fig. 77.

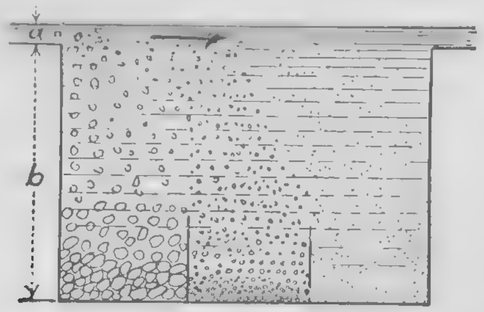


FIG. 77.—Settling Box.

The stream of water brings in the pulverized material through a shallow trough which empties into a comparatively deep box.

The box is so designed that the water has a fairly uniform horizontal velocity throughout. The larger particles drop down rapidly into the first compartment in the bottom, while successively smaller particles are carried farther and farther horizontally, into different compartments, before they finally reach the bottom. The finest particles are carried over the edge of the box before they have time to settle.

To make separation efficient, several points must be observed: the distance b must be large compared with a, otherwise particles coming in at the top of the stream would go into a more distant compartment than those of the same size entering at the bottom; the feed should enter smoothly and without any considerable velocity in any direction; the horizontal current in the box should be steady and fairly uniform.

Very frequently this method, using either air or water as the fluid, is used to divide the pulverized solids into but two classes, the finer of which is carried over the side, while the coarser remains in the box. Since V in the formula, $V=k\sqrt{D}$, represents the *relative* velocity of fluid and solid, another way to accomplish the same separation is to employ a rising current of fluid with a velocity just greater than the free-falling velocity of the largest particles which it is desired to remove. These particles and smaller ones will then be carried up and out, while the larger ones settle slowly.

Probably the greatest use for this method of separation into two parts is in connection with the operations of crushing and grinding. As was pointed out under the discussion of the factors controlling the efficiency of fine grinding, it is essential for the best results that each particle be removed from contact with the grinding surfaces and carried out of the machine as soon as it has become sufficiently small. In many stamp and pebble mills this is accomplished by passing a stream of water through the mill to carry away the fines in accordance with the principles above enunciated. Screens are usually employed to prevent the removal of particles not yet ground fine enough. Perfect separation by settling alone is impossible on account of the eddy currents caused by irregular cross-section and the motion of the grinding mechanism.

A blast of air is also used to effect the same sort of separation in various types of pulverizers. Screens are sometimes used

here also, but they tend to clog, and it is often found better to separate out the oversize particles by enlarging the cross-section of the air duct and in this way reducing the velocity sufficiently for the large particles to separate out and be returned to the mill, while the smaller ones are carried on to larger settling chambers, bag filters, etc.

An example of separation by means of screens is found in the Fuller-Lehigh pulverizer, p. 300. In machines of this class a rapid circulation of air is obtained by attaching four blades to the main rotating shaft which constantly lift the fine particles from the zone of active crushing through a fine screen set around the upper or "separator" portion of the mill. Particles too coarse to be easily carried through this screen are returned by gravity to the further action of the crushing rolls.

The Raymond roller mill, Fig. 71, illustrates the utilization of air separation of the fine particles as soon as formed as a means of increasing the efficiency of grinding. A continuous current of air is drawn up between the crushing surfaces into a well-designed separator placed immediately over the mill. The diameter of the separator increases rapidly as it rises so that the velocity of the air current decreases and allows the larger pieces to fall back into the grinding zone directly. At the top of the separator the air current is deflected into an interior cone where further separation takes place—that which fails to stay in suspension falls again into the mill proper. Such a grinding device requires a very perfect separator to arrest the product in the receiving chamber; mechanism for this purpose will be described on p. 331.

There are a number of very efficient machines now on the market, built independently of any grinding apparatus, based upon this principle of air separation. The material passes first into a constricted area in order that a high initial velocity may be imparted to it. The cross-sectional area of the separator must then rapidly increase, allowing the air velocity to fall. Only those particles which at the lowest velocity maintain a frictional resistance greater than the downward thrust due to gravity are carried out of the separator into the final collector.

B-1. SEPARATION DUE TO DIFFERENCE IN SPECIFIC GRAVITY

The separation of material which is composed of substances having different specific gravities presents a problem which has been worked out in much detail in the broad and important field of metallurgy. As a rule, the ore or valuable part of a mineral deposit possesses a specific gravity different from the worthless part or gangue, and it would seem a relatively simple task to effect a separation by making use of the difference in the velocity of fall through a resisting medium as given by the expression

$$V = k\sqrt{\frac{D(S-s)}{s}},$$

where S is different for the two constituents. Three important difficulties, however, are met. *First*, the dimensions D for all particles in the lot to be separated must be very nearly the same, and the close screening of the raw material required to accomplish this result is relatively expensive. *Second*, it generally happens that a certain percentage of the grains crush in such a way that each individual is made up partly of mineral and partly of gangue; its specific gravity is therefore between that of each of the constituents. *Third*, a certain percentage of the crude ore is crushed so fine that the particles no longer obey the ordinary laws of falling bodies and form so-called "slimes" which refuse to classify according to their specific gravities.

Free Settling.—From the relationship between linear dimensions and specific gravity already noted it follows that two bodies of different dimensions D and D_1 and of different specific gravities S and S_1 when falling through a medium of specific gravity s will attain equal velocities when the inverse ratio

$$\frac{D}{D_1} = \frac{S_1 - s}{S - s} \quad \ldots\ldots\ldots (1)$$

is satisfied. Therefore these dimensions are the limiting values which particles of two substances with specific gravities S and S_1 can have if separation by falling through the medium is to be carried out. So long as the ratio is less than this, the smallest particle of the heavier substance will attain a final velocity greater than the largest particle of the lighter substance, and separation is

possible. Hence, if a pulverized mass be sized by passing through a set of screens, the fraction on any one screen can be separated into its own components by settling, if the ratio of the largest particle to the smallest is not greater than is indicated by Equation (1). Obviously, however, the more nearly these particles are of the same dimensions, the more nearly equal will be the frictional resistance of falling, and hence the greater will be the difference in the rates of fall. The ratio of the size of opening or mesh in the larger screen to the next smaller is called the sieve scale and has already been discussed on p. 308. It is clear that the selection of those screens which must be employed will differ for each set of substances and is determined by Eq. (1). For practical purposes when water is the fluid medium this may be written $\frac{S_1-1}{S-1}$ and when air is used it becomes $\frac{S_1}{S}$. It is evident therefore that when the specific gravities are not widely different the sieve scale must be considerably smaller for separation in air than for separation in water. The ratio of the diameters of grains of a number of minerals having equal ratio of the falling velocities, or as is more accurately described, equal free settling velocities, has been determined by Richards.[1] From a number of analyses of quartz and galena ranging from grains having diameters from 2 to 0.5 mm., this ratio of diameters was found to be from 3 to 3.7. That calculated from Eq. (1) is in this case about 4, the specific gravities being 2.65 and 7.5, respectively. It is sometimes expedient to use water for the liquid medium, and yet have s assume a value greater than unity. This can be done by suspending in the water a material so fine that the mixture behaves as a liquid with a specific gravity materially greater than water. This principle seems not to have been sufficiently applied to determine its real value.

Since quartz and galena differ more in specific gravity than the majority of ores, in general, excessively close screening would not be necessary in order to make possible a satisfactory separation by free settling. Another objection to this method lies in the fact that if "free settling conditions" (that is conditions such that there is practically no interference between

[1] *Trans. Am. Inst. Min. Eng.*, **1894**, 409.

the falling particles) are to be maintained in any apparatus, the capacity of a given separating system for solids must be rather small compared to its volume. For these reasons a modified system of separation known as hindered settling, is very much used in metallurgical work.

Hindered Settling.—There are a number of methods of separation which, while markedly different in apparatus and details of operation, nevertheless involve the same basic principles of hindered settling. This may be defined as settling under conditions designed to crowd the particles close together and cause interference between them.

Two principal advantages are found common to almost all the variations of this method;

First.—It greatly increases the capacity of any separating system, and

Second.—It sets up a new scale of "equal hindered settling particles" where the ratio of the diameters of the light and heavy particles which settle at the same rate is often nearly twice as great as before. This renders possible either a much more perfect separation for a given set of conditions or a satisfactory separation with a wider range of sizes. In this connection it is evident that the continual interference and agitation to which the grains are subjected in hindered settling prevents the formation of agglomerates by the small particles which would then be classified with the larger sizes.

Hydraulic Jig.—The increased ease of separation obtained with hindered settling is due to several causes which may well be considered in the operation of a *jig*, one of the simplest and most widely used of all hydraulic separators. Fig. 78, p. 322, shows side and end sections of a single compartment in a series of wooden jigs. The plunger has a fairly rapid reciprocating motion which keeps the water going up and down through the sieve. Assume that the feed contains particles of galena (sp. gr. 7.5) and quartz (sp. gr. 2.65) which separate into four groups.

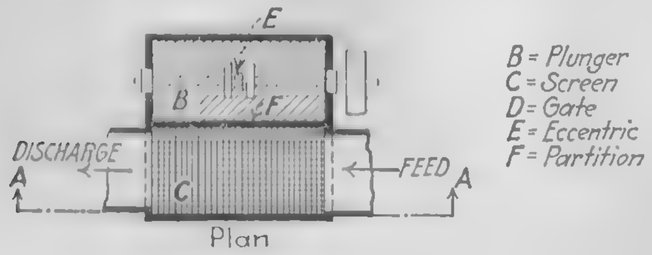
1. *The tailings*—medium and fine particles of quartz and very fine particles of galena, which pass out with the effluent water to the next compartment.

2. *The middlings*—large particles of quartz which form the top layer of the bed of ore on the sieve, mixed with some medium-sized galena which has not yet worked its way through to the

bottom. Middlings are raked off intermittently and sent back to be recrushed.

3. *The coarse concentrate*—galena particles too coarse for the sieve, which form a layer just above it. They may be removed automatically or raked off after the middlings. A few pieces are always left to form a bed for the next run.

4. *The fine concentrate*—small particles of galena which have passed the sieve and collected in the hopper. This is the chief product of the jig and is taken out through a gate in the side of the hopper.



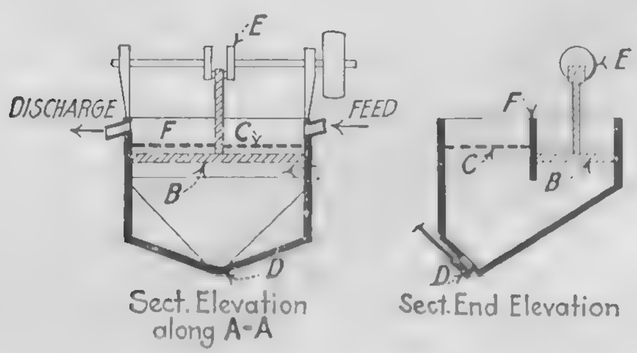


FIG. 78.—Hydraulic Jig.

It is evident that the bed of middlings which is kept in a state of agitation or "teetering" operates somewhat as a screen, allowing small galena particles to slip down through the channels but refusing the larger quartz, which has, however, the same free settling velocity.

Another effect is added to this screening when the upward rush of water lifts the mass of particles off the screen. The heavier particles then drop through the fluid, and under such conditions of "teetering" the specific gravity of the mixture of water and sand is greater than that of water alone. This average

specific gravity would be recorded by a hydrometer placed in the suspension, since a mixture of water and sand would be displaced, but it must be realized that to obtain an average specific gravity greater than unity the particles must be heavier than water and must be suspended in water, not at rest on the screen. As a corollary to this it follows that the particles must have a downward velocity relative to the water. This greater specific gravity increases the ratio of diameters of equal settling particles so that much better separation is possible. Richards[1] calculates his hindered settling ratios for quartz and galena by using the average specific gravity of the sorting bed which is 1.5. Under these conditions

$$\frac{D}{D_1}=\frac{S_1-s}{S-s}=5.2,$$

compared with 3.9 for free settling, which checks fairly well with the results of his experiments.

The function of the pulsating or upward moving current is not to separate the particles by any difference in the acceleration given to the different sized particles (as sometimes stated) but solely to keep the particles in suspension and thus increase the apparent density of the separating medium.

Jigs are used extensively on relatively coarse materials and to some extent on finer products.

Wilfley Table.—Various types of riffles are employed for the separation of fine sands, the simplest type being constructed of blocks or bars across the bottom of a sluice-way. The Wilfley table usually consists of a nearly horizontal table with parallel cleats or riffles along its surfaces, equipped with an eccentric and springs or similar devices at one end to give a longitudinal jerking motion to the whole. The ore is fed at the highest corner and water from a pipe along the upper side floats the lighter particles with it across the table while the heavier mineral is caught by the riffles and carried down the length of the table by the jerking motion imparted to it.

The Vanner, which is used for sands and slimes, consists of an endless belt running up a slight incline which is given a shaking motion in the plane of the belt. Water flowing down the belt removes the lighter mineral while the heavier is carried to the upper end and discharged.

[1] *Loc. cit.*, p. 320.

Hydraulic Classification and Hydraulic Separation

From the preceding discussion of free and hindered settling it should be clear that to effect the separation of two admixed solid materials of differing specific gravity it is necessary that the ratio of diameter of the largest particles of light material to that of the smallest particles of heavy materials shall not exceed a definite value, a value which is greater in the case of hindered settling than in the case of free settling, but still definite and not very large. It is, therefore, imperative that hydraulic separation be preceded by some sort of a sizing operation and obviously screening is the sizing method that first suggests itself. It has already been pointed out that screening is an expensive operation and one in which the exact control of sizing of particles is difficult to realize. Expense and difficulty of sharp separation in screening increase very greatly as the particles to be separated decrease in size. Thus, screening operations below 20-mesh become almost impracticable on a commercial scale. It is, therefore, necessary to substitute for screening some cheaper and better sizing method.

Hydraulic Classification.—The method employed to avoid the difficulties of exact sizing by screening of fine materials in large quantities is to subject the materials in question first to a separation by *free settling*, the fractions obtained by this method being then subsequently separated into the component materials by hindered settling. If a mass of two materials, the particles of both of which vary in size between definite but widely separated limits, be subjected to free settling, the materials can be broken up into fractions; the fraction containing the largest particles can be made to consist of the heavy material only; the fraction containing the finest particles can be made to consist of the light material only; but in all intermediate fractions the largest particles will consist of light material only and the smallest particles of heavy material only, while the intermediate sizes will consist of particles of both materials.

If now each fraction obtained by free settling has been so controlled that the ratio of diameters of the largest particles in that fraction to the smallest does not exceed the hindered settling ratio for the two materials, these fractions obtained by free settling may be subjected to hindered settling, securing thereby complete separation of the material.

Preliminary free settling, utilized as above outlined to secure the sizing of the particles to be separated preliminary to the final separation, is spoken of as hydraulic classification. The subsequent separation by hindered settling is described as hydraulic separation.

Hydraulic *classification* is less efficient than screening in that in each fraction the particles of both materials are not uniformly graded from the smallest sizes to the largest, but, as stated above, the largest sized particles are of light material only. The amount of heavy mineral obtained by subsequent hydraulic *separation* is, therefore, less in the former case than would have been obtained by treating the screened fractions. On the other hand, the avoidance of the difficulties of screening operations, especially for fine fractions, so far outweighs this disadvantage that hydraulic classification as a means of sizing preliminary to hydraulic separation is very widely used in mining practice.

Spitzkasten.—Possibly the oldest classifying device and one yet much in vogue, is called a Spitzkasten. In its simplest form it consists of a series of inverted pyramidal or conical boxes, and with each succeeding box both larger and deeper than the first. (Fig. 79.) The "pulp" (as the mixture of fine raw ore and water is called) is allowed to flow in at one edge of each box and across to the opposite side and into the next box. The increasing cross-section and depth produces a decrease in the rate of flow as the mass passes from the narrow to the broad end, and thus a more or less complete separation is effected. The classified ore is drawn off at the apex of each box, while the very fine, almost colloidal particles or "slimes" flow from the top of the last box to suitable collectors. Most modern classifiers introduce at the apex of each box an additional stream of water known as "hydraulic water." By this means not only is a sharper classification obtained, but a considerable measure of concentration, that is, separation of the heavier mineral from the lighter gangue, is effected. Obviously a great number of variations and modifications can be introduced into such a type of apparatus; but if the principle be understood, the different factors may be changed to suit the conditions at hand. Coal-washing machines operate on this principle, but in this case it is the valuable part which floats off, while the slate and pyrites settle out first; moreover the coal has already been screened and in this case the apparatus operates as a separator.

Dorr Classifier.—When it is necessary to separate a relatively large amount of fine material from coarse, as in classifying the

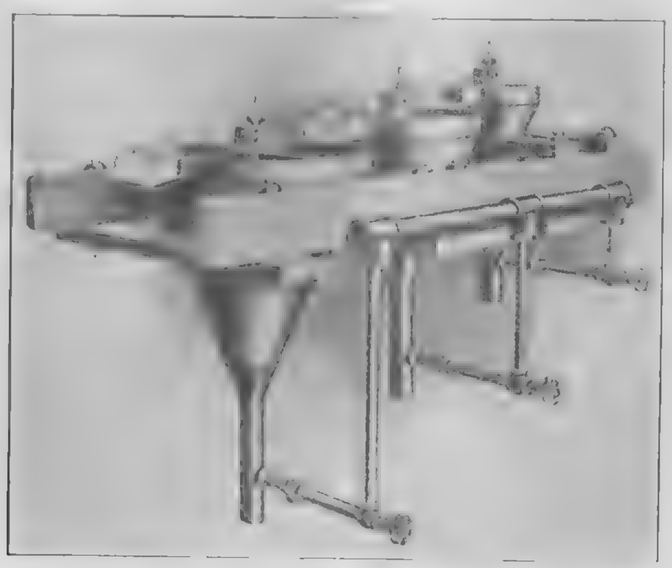


FIG. 79.—Spitzkastens.

product of a tubemill grinding in water involving, however, no separation of materials, machines of special design are available.

FIG. 80.—Dorr Classifier.

As an example can be noted the Dorr classifier, Fig. 80. This machine consists of an inclined settling box in which the heavy

material which a predetermined current of water fails to carry over the discharge end is continually removed by the action of mechanically operated rakes which push it up the incline. The heavy material goes again to the pulverizers, while the slime is ready for treatment.

An important use of the Dorr classifier in the chemical field is for the counter-current extraction of solids by liquids.

B-2. SEPARATION DUE TO TEMPORARY CHANGE IN SPECIFIC GRAVITY, FLOTATION PROCESS

The apparent specific gravity of a material of porous structure (such as crushed coke) is much less than the real specific gravity of the solid, due to air which is entrapped in and around the particle, and frequently a relatively heavy material, even though coarse, may be made to float on water. Some substances, notably the metallic sulphides, possess the peculiar property of assuming a false specific gravity due, apparently, to their lack of adhesion to water and their ability to hold on themselves or to attach themselves to, a film of air or other gas. If properly introduced onto a moving current of water, the valuable sulphide may be floated away from the gangue even though much heavier than the gangue. This ability possessed by the metallic sulphides to cling to an air bubble and to be in this way transported to the top of the current and thus separated forms the basis of a most important method of mineral concentration known as "flotation." The selectivity or "preferential affinity" of the mineral for the air bubble, as compared to the affinity of the particles of gangue for the air bubble, can be greatly increased by the addition to the admixture of crushed ore and water (pulp) of a very small amount of a large variety of substances, mostly organic in nature. Thus as little as 0.1 lb. of such widely differing compounds as the insoluble diazo-amino-benzene or the very soluble sodium-ethyl-xanthate, to 1 ton of ore suspended in 5 tons of water effects a recovery of 93 per cent of the copper sulphides when contained in an ore carrying as little as 1 per cent of these minerals. In order to form bubbles of sufficient permanency to hold the sulphides until the mineral-bearing froth can be removed, a very small amount (0.2 or 0.3 lb. per ton) of certain oils, for example, steam-distilled pine oil, is also added to the ore-water mixture.

The air bubbles used to transport the mineral to the top of the containing vessels are produced within the pulp either by beating in air through violent agitation, or by forcing air into the pulp from below through a porous membrane; sometimes a combination of both methods is employed.

The device used to effect separation in this way is generally a series of compartments of the Spitzkasten type in which the gangue sinks to the bottom and eventually is discarded while the valuable mineral is drawn off into separate channels and finally recovered by use of a continuous vacuum filter. This method of concentration has proved to be a most valuable one for sulphide ores of quite diverse character. There obviously exists the possibility of converting oxides or carbonates, which in themselves refuse separation, into the corresponding sulphides and subsequently separating by this flotation principle.

A number of different flotation processes are in successful operation, but none of the many theories advanced to explain the observed phenomena has yet been generally accepted as applicable to all cases.

C. OTHER METHODS

1. Separation Due to Magnetism.—The attraction which an electro-magnet has for many metallic bodies has long formed the basis of a method for removing such substances from comminuted or ground material. Thus rags before being fed to a pulp digestor, or grain before milling, can be freed from adventitious particles of iron by passing the stock in a thin stream over a rotating magnet. The same principle may be employed in separating finely ground minerals which are more or less magnetic, from the gangue which is non-magnetic. Separation may be effected by subjecting the pulverized material to the influence of the magnet in four ways.

1. Separation by deflection while falling through air.
2. Separation by deflection from a moving belt.
3. Separation by adhesion to the moving magnet.
4. Separation while suspended in water.

Machines are available constructed on each of these four plans.

2. Separation Based upon Electrical Conductivity.—When a particle, itself an electrical conductor, comes into contact with a highly charged surface, it instantly assumes a charge of the same sign, and is strongly repelled from the surface. If a non-conductor of electricity, the particle remains on the surface until it is removed, either mechanically, or by the withdrawal of the support. Although theory requires only that one substance be a better conductor than the other to make separation possible, practically this difference must be quite appreciable. If, however, the mass be charged to a high potential of the sign opposite to that of the separator surface, the better conductor is more quickly discharged and again charged with the sign of the surface and repelled, while the poorer conductor adheres to the surface for some longer interval of time, and thus a sharper separation is made possible. The Huff electrostatic separator is a good example of this type of apparatus; its principle is shown in Fig. 81.

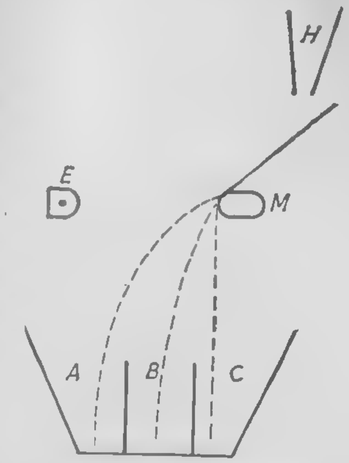


Fig. 81.—Huff Separator.

Huff Separator.—The fine mix feeds from a hopper *H* onto a metal plate *M* which is grounded. A copper wire at high potential inside the wooden electrode *E* gives a strong silent discharge between *E* and *M*. The better conducting particles *A* are more influenced by this discharge and drawn out further towards *E* while the poor conductors *C* drop directly. A mixture of *A* and *C* is collected in compartment *B*.

Electrostatic separation is a process which would seem to have an unique principle not yet fully developed.

PART II. SOLIDS FROM GASES

Settling Chambers.—Owing to the relatively slight resistance offered to the fall of a solid body by gas, difficulty in separation of the two is encountered only when the solid is so finely divided that the area of each particle is very large compared to its mass. For a great many years a simple settling chamber was all that was

employed for most cases. Such an apparatus is generally a rectangular box of such dimensions that the volume of gas may pass through at a relatively low velocity. Obviously the rate of passage must be sufficiently slow to allow time for the smallest particle of solid which is to be removed to fall from the top of the chamber to the bottom; if it does not reach a support before it arrives at the end of the chamber, it is again caught up in the gas current and swept out of the chamber. But such a simply constructed chamber is generally fatal to efficient separation if the volume of the gas to be handled is large. It can be seen, however, that it is but necessary to shorten the path through which each particle must fall in order to reach a lodging place, in order to increase the capacity and efficiency of such an apparatus. This can be done by providing the chamber with a series of parallel shelves running lengthwise. Little resistance to the flow of gas is thus introduced,[1] while the lodgment of each particle of solid of a given size is assured before the exit end of the chamber is reached. It is necessary to pass substantially an equal volume of gas between each of the shelves in order that the apparatus may be operated at its maximum capacity. The Howard Dust Collector embodies the above principle and ensures an even distribution of gas automatically in this ingenious way. Such separators are admirably adapted for burner and roaster gases and are quite extensively employed.

Centrifugal Separators.—Instead of gravitation, centrifugal force may be used to separate the solid particles out of the gas current. While the force tending to throw the particles away from the center may be made very great by maintaining a high peripheral velocity, provision must be made for withdrawing the separated dust from the sides of the container without allowing it to be again caught by the incoming gas.

In the dust collectors of the Knickerbocker Co., there are utilized a number of devices for increasing the efficiency of the apparatus, which indicate the modifications which the principle of separation by centrifugal force may take.

The separator consists of two concentric vertical cylinders provided with a bottom cone for receiving the product and a pipe at the top leading to the fan. Dust-ladened gas enters the inner

[1] This is true, despite the great decrease in hydraulic radius, since in any case the gas velocity is very small.

cylinder tangentially and is given a rapid whirl as it passes around the chamber and then up and out of the fan. The solid particles are thrown against the walls of the chamber and escape with some of the gas through vertical slit-like openings into the annular space between the cylinders. Here a much less rapid whirling motion obtains which allows the dust to settle on the walls of the chamber and bottom cone, while the gas passes up into the dust-free vortex and out through the top. When the dust collects in sufficient quantity it slides down the walls to an automatic discharge trap at the bottom. When such an apparatus is placed between an exhaust fan and the source of dust, as an emery wheel, tumbling mill, or sand blast, a slight vacuum is maintained in the chambers. By removing the solid particles before the gas current reaches the fan, deterioration of the latter due to abrasion is, of course, practically eliminated. The Raymond apparatus, p. 302, separates the fine product from air by centrifugal force in a similar manner.

Bag Filters.—The fact that solids as small as ordinary bacteria may be separated from air by passing it through a layer of cotton wool or heavy loosely woven cotton cloth indicates the efficiency of a filter medium of this kind. Doubtless the removal of the bacteria is due more to their impact and subsequent adherence to the fibre than to a screening action; but this principle may be used both when a large amount of very fine particles is to be removed from a limited amount of gas, as in the manufacture of zinc oxide, or when a very little solid is taken from a large volume of gas, as in the filtration of air. Bag filters are simple of construction and find considerable use in the zinc industry and in other cases when the particles are very fine and centrifugal separation is not applicable. A very compact dust collector using cloth bags is offered by the Raymond Pulverizer Co. of Chicago. This may be made of any size to suit the capacity required.

Separation by Impact with Water.—Separation occasioned by letting the gas and solid particles come in contact with a wet surface on which the particles will cling may be made very effective. By having the liquid actually flow over the impact surface the solids are not only caught out of the gas, but are continually carried away. An important element in design in any gas-cleaning device of this kind is to provide for a constant deformation of the gas volume as it passes through the apparatus.

Thus a gas bubble may carry in suspension fine particles of a soluble salt and yet pass through water with the loss of only the relatively small portion of the solid which is near the surface of the bubble. It is only when the bubble is split up or deformed that the portion originally at the center can be brought in contact with the dissolving or adhering medium and a cleansing of the gas be effected. The gas washers at Gary illustrate this principle.

Instead of having the gas impinge upon a wet surface the action can be reversed and drops of a liquid may be moved through the gas. Thus, very effective cleansing can be obtained if a fine spray of water be forced through a current of gas moving in an opposite direction. Apparatus operating upon this principle has been introduced by the Carrier Co. If the dust be very fine, however, much will pass any of these washers when the velocity is high. The fact that upon condensation a vapor will deposit first upon dust particles as nuclei may be utilized in depriving a gas of all its dust. By saturating air with water vapor and then condensing out a portion, the dust particles are carried down.

Cottrell Separators.—A very novel and efficient method for separating very fine particles of solids or liquids from a gas has been developed by Cottrell. Gas molecules can be ionized by α, β and γ rays and the brush and corona discharges from high potential electrodes. The gas is thus ionized in Cottrell's apparatus by passing it between a series of electrodes which maintain a silent or glow discharge. The very small dust particles are given an electrical charge by contact with the ionized gas and collect together. As the gas and dust pass further along they come under the influence of a second series of electrodes with rectified high voltage discharge. The dust aggregations are attracted to one of these electrodes and deposited there.

PART III. LIQUIDS FROM LIQUIDS

Decantation.—The means employed for separating one liquid from another depends upon whether or not the two liquids are miscible. If they are not, and do not form an emulsion, it is only necessary to provide an opportunity for the two to separate into layers, according to their specific gravities, and to draw these

two layers off from different levels. For intermittent separation a discharge pipe set in a swivel joint inside the tank is very convenient. This may be a joint of special design or the level leg may be held in a nipple. The end of this pipe may be either attached to a float, which insures the inlet end of the pipe being always just a little below the surface of the liquid, or may be lowered by a chain.[1] Instead of a rigid pipe on a swivel a flexible tube attached to the exit pipe may be employed; the inlet end here also may be raised and lowered at will, or be carried in a float. For continuous separation, as in the distillation of an oil with steam, a separator consisting of two compartments with connections is convenient.

If the two liquids are so nearly the same in density that they do not easily separate, it is sometimes expedient to add a substance soluble in but one in order that it may acquire a specific gravity materially greater than the other.

Centrifugal Force.—If the force of gravity alone is not sufficient to separate two liquids, as is the case in many emulsions, or if separation by gravity be too slow, centrifugal force may be employed. When the mixture is fed into a container which is rotating at a high rate of speed, the heavier liquid is thrown to the outside of the vessel, while the lighter remains in the center. The two vertical layers will rise to the top of the rotating vessel as the operation continues, and by suspending a diaphragm into the dividing lines, the two may be drawn off from separate exit spouts. The DeLaval cream separator, was the first apparatus designed for this purpose and its extensive introduction has revolutionized the milk industry.

When the liquids are miscible, separation as a rule depends upon a difference in the vapor pressure of the constituents. The utilization of this property is the basis of the operation known as Distillation, which is so important as to require for its treatment a separate chapter.

Other Methods.—Sometimes the solvent power of one liquid for another can be so changed by the addition of a third body as to make separation possible. Examples of this are the separation of ether and water and of methyl alcohol and acetone by the addition of a material which will depress the solubility of one liquid in the other.

[1] See Fig. 82, p. 338.

PART IV. LIQUIDS FROM GASES

Entrainment.—When liquids are carried in suspension by gases the phenomenon is generally spoken of as entrainment and usually occurs as one of the factors in a more general problem. When a gas is formed from a boiling or decomposing liquid it is not uncommon to have some of the liquid carried out of the container by the gas in the form of a fine spray from the bursting bubbles. Thus in steam boilers finely divided liquid water is sometimes carried with the water vapor, and also in the destructive distillation of substances such as soft coal, the coal gas will carry with great tenacity a small portion of liquid tar. Separation in these cases depends largely upon the principle of having the drop of liquid hit and adhere to a solid surface or baffle plate. This may or may not be wet and self-cleansing as in the apparatus already described for separating solids from gases.

Dissolved Gases.—From a practical standpoint, gases are carried by liquids only when in solution and are separated either by

a. Chemical combination and precipitation.
b. Inducing the gaseous constituent to assume the vapor phase.

The means of accomplishing separation according to the first method are so simple and so closely allied to separation of solids from liquids as to need little treatment here. Thus hydrogen sulphide is removed from water by adding a little ferrous sulphate, and carbon dioxide separates when a slight excess of calcium hydrate is introduced.

The second method requires a disturbing of the equilibrium existing between the gas and the liquid. This may be done by heating the liquid, thus lowering the solubility, or by passing an insoluble gas through the liquid, thus sweeping out the gas, or by placing the liquid under a vacuum.[1]

PART V. GASES FROM GASES

A mixture of gases may be more or less completely separated by three methods.

[1] See Chaps. XVII, XVIII, and XIX.

(*a*) Rate of diffusion through a membrane.
(*b*) Selective absorption and adsorption.
(*c*) Fractional condensation.

Diffusion.—According to Graham's law, for a given membrane, the linear velocity of the diffusing gas is directly proportional to the difference in partial pressure of the gas in question between the two sides of the membrane and to the square root of the absolute temperature of the gas, and inversely proportional to the thickness of the membrane and the square root of the molecular weight of the diffusing gas. The coefficient of proportionality is determined experimentally for each material, and is doubtless a function of the percentage of voids in the membrane. Although it is easy to carry out such separation experimentally, no technical method of importance has as yet been introduced. It would seem that a valuable field of work lies here untilled.

Selective Absorption and Adsorption.—The separation of gases through the principle of selective *absorption* is well illustrated in the modern methods of gas analysis, and is of wide application. The most important factor in the design of the apparatus for this purpose is that which provides for the complete mixing of the absorbing liquid and the gas.

The principles of operation here are essentially those of the absorption of gases which are taken up elsewhere.

The use of solids in the selective adsorption of gases is illustrated by the army gas mask.

Fractional Condensation.—While theoretically it may be possible to separate two gases by applying such a pressure and temperature that one will condense to a liquid, and not the other, it is found in practice easier to condense the gaseous mixture as a whole, and subsequently to separate by fractional distillation. The treatment of this method of separation will be found under Distillation. Examples of this method are seen in the recovery of oxygen and nitrogen from the atmosphere, or of helium from natural gas.

The many important devices which are in use for separating suspended solids from liquids may be studied under two general heads. *First:* those in which the liquid is still and the solids move through it and settle to the bottom of the container by the

force of gravity. *Second:* those in which the liquid passes through a porous membrane of such character that the solid is retained. The membrane may be of the most diverse character and varies from a tower filled with coarse charcoal to a plate of unglazed porcelain of almost microscopic openings. A further classification may be made according to the character of the force which drives the liquid through the membrane.

a. Sedimentation.—As has been shown, the factors which control the movement of a solid body through a resisting medium are the size and specific gravity of the particle, and the density and viscosity of the medium.

The viscosity of the medium may be greatly changed by a change in its temperature, and the rate of sedimentation thus modified. Manifestly, if the individual particle could be made larger the frictional resistance would be decreased and sedimentation would follow. This may be accomplished in two ways: *First,* by inducing the large particles to increase in size at the expense of the smaller ones by agitation. Since a small particle has a greater solubility than a large one, the solution acts as a medium by which the material composing the small one is transferred to the large one.[1] *Second,* by bringing about an aggregation of the fine particles into larger units either through the addition of an electrolyte which will destroy the colloidal condition, or some substance capable of forming a voluminous precipitate which will entrap and drag down with it the very fine particles. The size of particle varies considerably in a suspension, but the rate at which the upper surface of the suspension settles is determined by the size of the smallest particle in it. If the range of particle size be not too great, the line of demarkation between sediment and supernatant liquid will in general be clear, becoming indistinct, however, if the percentage of the smaller particles is low.

The general laws according to which sedimentation takes place, a knowledge of which is necessary in order to design apparatus which shall operate most efficiently as to time and material, have been investigated by Rollason.[2]

[1] Since solubility usually increases with temperature, heating hastens the coagulation of a precipitate and hence its sedimentation. It also helps by decreasing viscosity.

[2] Undergraduate Thesis, M. I. T., 1913.

It has been found that the settling of a solid through a fluid takes place in three stages—the first stage being known as *free settling,* the second as a *transition period,* and the final stage as *impeded settling.* The rate of settling during the first stage is constant, *i.e.,* if the top of the sludge drops 1 ft. in one 20-min. period it will drop the same distance in the next 20 mins. When the particles of the sludge have settled to such a point that they begin to interfere with each other's motion the rate of settling decreases. This condition is reached when $\frac{h}{h_0}$ reaches a certain value determined by the character of the suspended solid, where h is the height of the sludge at the time the rate is measured and h_0 is the final height to which the sludge will settle after a very long time has elapsed. The rate during this transition stage gradually falls until a point is reached where $\frac{h}{h_0}$ equals a second constant. Then impeded settling begins and the rate may be calculated from the expression, $-\frac{dh}{d\theta}=k\frac{h-h_0}{h_0}$. From this it follows that, during both free and impeded settling of a given suspension, the time necessary to drop between two fixed values of h/h_0 is proportional to h_0. During the transition period this relationship continues to hold, which, in turn, simplifies quantitative design.

In an intermittent sedimentation tank, the clear liquid must be drawn off to as near the surface of the solid as possible without disturbing it. This may be done by a series of draw-off cocks fitted down the side of the tank at different levels. For large tanks a draw-off tube such as is shown in Fig. 82, is most serviceable and easily constructed. Or, a bent tube entering the tank through a packing box and a swivel joint and turned from the outside, is a very satisfactory device for drawing off the liquid to a predetermined level.

Dorr Thickener.—If the sedimentation tank is to be continuous in its action, provision must be made for allowing the liquid at some part of its path to come almost to rest in order that the solid may become attached to a support; or to allow the solid to drop from the moving part of the fluid into a portion which is still and from which it may further separate slowly. An example of this type of apparatus is the Dorr thickener, Fig.

83. This consists of a large, shallow, cylindrical tank into which the slurry is fed at the center. The solid material gradually settles to the bottom and the clear liquid overflows through openings in the periphery of the tank. The tank is fitted with

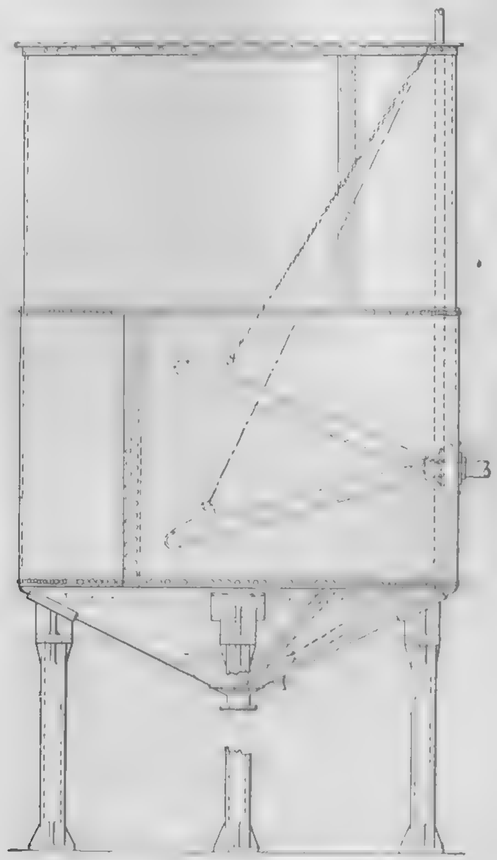


FIG. 82.—Decantation Tank.

rotating arms carrying plows which rake the settled material towards the center of the bottom where it is discharged through an opening with the aid of an ejector or pump. It would seem as though devices of this type might find considerable use in the chemical industries where *decantation* of a clear supernatant liquor with filtration of the resultant sludge would be more used if it were not for the time consumed.

In order that the time required for solid matter to settle out of a liquid may not be excessive, the path which the solid particle

will travel before finding a lodging place must be short. The deposition of the sediment will, however, quickly interfere with the gentle flow of the liquid over the surface of a narrow channel, if some provision be not made for automatically removing the deposit. Apparatus of this type has found its greatest development in the art of water purification, especially the softening of boiler feed water. A good example of such structure is found in the Kennicott Continuous Water Softener where the boiler

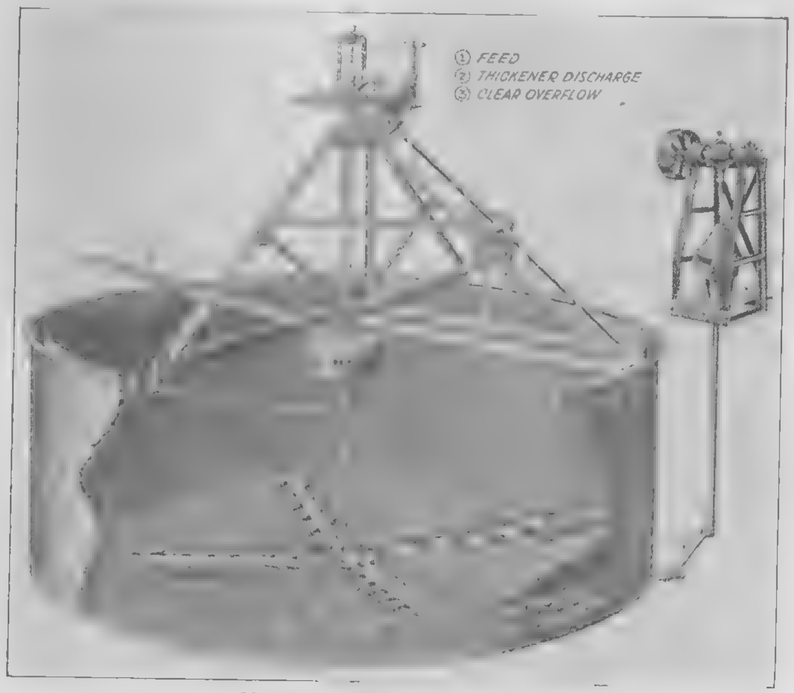


FIG. 83.—Dorr Thickener.

feed water, after having been mixed with lime and soda, is pumped into the bottom of the apparatus which consists of several perforated cones placed one above the other in a cylindrical tower. The water containing the suspended solids passes through the perforations, the solid being deposited in the cones and settling down into the bottom of the tower.

When gravitation does not supply enough force to separate the solid from the liquid *by sedimentation*, recourse may be had to centrifugal force. Although not used for this purpose to a large extent in industrial work, a "centrifuge" capable of a very

rapid rotation is indispensable in a well-equipped laboratory. The rotating element may take the form of a frame holding a series of glass tubes in which a number of liquids may be placed, or a cylinder with a solid wall against which the solid is thrown.

Flotation.—Manifestly when a suspended solid is lighter than the liquid, it can be collected at the top of the liquid and either skimmed or floated off. Frequently efficient and complete separation of fine particles requires the aid of a sort of bombarding effect of fine air bubbles ascending from the bottom. The particles are thus propelled upward and tend to coalesce with the mass at the top. This method frequently commends itself when handling greases, fats, gums, and material of this kind: materials which do not lend themselves to other methods of separation.

b. Filtration.—This subject is of such importance that the succeeding chapter is devoted to it.

CHAPTER XI

FILTRATION

General Considerations.—Filtration is the process of separating suspended solid material from a liquid by forcing the latter through the voids of a porous mass called the filtering medium. The two important variables to be considered in the construction of a filter are therefore the material which forms the separating medium and the method used for forcing the liquid through this medium. It is obvious that the latter will be largely determined by the resistances to flow offered by the former. When this resistance is relatively small the force of gravitation is all that is required, and such an apparatus is known as a "gravity filter." If gravity is not sufficient, the pressure of the atmosphere may be allowed to act upon one side of the filtering medium, while it is withdrawn from the other side; such a device is called a "vacuum filter." But a filter of this type is limited to 15 lbs. pressure per sq. in., therefore, if greater force be desired a positive pressure in excess of the atmosphere is applied to the liquid mixture by means of a pump on the other side. This may be a heavy air pressure upon the supply reservoir, usually in the form of a "monte jus," or the liquid mixture may be forced directly by a pump against the filtering medium. This gives rise to the mechanism known as "filter press" of which there are a number of types. Finally one may employ centrifugal force to drive the liquid through the filtering medium; machines so operated are known as "centrifugals" or "centrifuges."

In a systematic treatment of filtration, however, it seems best to consider the different types of filters from the point of view of material making up the filtering medium, rather than the kind of force used in their operation. An efficient filtering medium may function in either, or all, of three ways: *First*, the size of the channels through it may be smaller than the size of the solid particles to be retained, and thus only the fluid can

pass through; *Second*, the channels may be larger than the solid particles but be of such a character that the solids will adhere to their walls and only the clear liquid will pass through; or *Third*, the channels may at first be larger than the solid particles, but of such a size that they will fill up with the solids to an extent that the openings finally become smaller than the solid particles. These solids may be the material itself or some "filter aid" such as kieselguhr, infusorial earth, fullers' earth, fine sand, wood pulp, calcium sulphate, calcium carbonate, etc. In this last case, the first liquid to pass the filter may not be clear, and the active life of the filtering membrane may be short; but in practice it is generally better to employ a rather coarse material and depend upon building up a desired filtering medium, than to employ a very dense cloth. The conditions which control the choice of a filtering membrane and the methods of forcing the liquid through it are so numerous that no general statement can be made. The controlling factors will be discussed as they appear in treating the types of filters now available.

CLASSIFICATION OF FILTERS

To satisfy most commercial conditions a filtering medium must be easily cleansed or cheaply renewed. Hence the construction of the filter must provide either for removing the porous membrane for cleansing and replacing it as a separate element of the structure, or for washing or re-forming the membrane within the apparatus. This latter class is generally applicable only when the proportion of solids in the liquid is small, and when it is not desired to recover the solids after their removal. Consequently filters may be classified according to their structure into:

1. Filters with a loose or granular membrane.
2. Filters with a felted or woven membrane.
3. Filters with a rigid, porous membrane.
4. Filters with a semi-permeable membrane.

(1) Filters with a Granular Membrane

The simplest form of filter is a containing vessel with a false bottom filled with a granular material sufficiently fine to arrest the material in suspension. The choice of substance must depend upon the character of the liquid to be filtered. For example, a deep layer of coarsely crushed charcoal has been found most efficient for removing the heavy tar from pyroligneous acid, the product of destructive distillation of wood. In this treatment the purification probably is accomplished more by the ability of the charcoal to absorb and hold back the tarry matter, than to the size of channels between the pieces of charcoal. For the removal of certain impurities in raw sugar syrup a filter of this type is frequently employed, but the phenomenon is in this case one of adsorption.

Box filters consist of a box with a perforated bottom usually covered with successive layers of coarse gravel, fine pebbles, and canvas or cloth respectively. Although these filters are generally of the hydrostatic head type, suction may be used or a cover may be provided and positive pressure used in the filtration. An iron grating is generally placed over the canvas so that the sludge may be removed by means of shovels without injury to the filter.

For most salt solutions fine quartz sand is ordinarily adopted in this type of filter, as it is practically insoluble, and quickly settles into a compact layer of uniform structure. For alkaline liquids crushed marble or a pure limestone is a most serviceable material. Suspended matter is arrested by such a medium partly by its inability to pass through the minute channels between the grains of the filter bed, and partly by adhesion to the grains. When cleansing is necessary a current of water may be passed backward through the filter. This operation is efficient only in so far as the filtering medium is broken up and uniformly exposed to the reversed current. To avoid the formation of channels and to loosen the entire mass so that the grains may rub against each other and so be freed from the adhering sediment, a current of air may be forced up through the mass together with the water. Or if such agitation be not sufficient, the mass may be broken up by a mechanically driven stirrer. The slow rate of filtration through sand requires a large filtering area.

(2) Filters with a Felted or Woven Membrane

When the amount of solid material in the liquid is large, or when it is desirable to recover the solid portion, a loose filtering

medium becomes inadmissible and a felted or woven fabric of fibers is employed. This fabric may be made from vegetable fibers such as cotton, hemp, or jute for weak alkalies; of animal fibers, such as wool or horse hair for weak acids, or mineral fibers, such as asbestos for strong acids, and finally the membrane may be made from fine metal wire for very strong caustic, or where a high pressure is demanded. The use of wire filter cloth is developing rapidly.

The simplest form for such a filter is a circular or rectangular box or container to the lower edge of which is firmly bolted a perforated bottom. The filtering cloth or other fabric is laid on this false bottom and extends out between the walls of the container and the bottom thus making a tight joint. By bolting to this false bottom an air-tight shell, vacuum may be applied and the pressure of the atmosphere allowed to force the liquid through.

It is easily seen that if a pressure of greater than 15 lbs. per sq. in. is desired, instead of attaching the shell to the false bottom, the container may be closed on top with a solid plate, and the mixture to be filtered forced into this chamber from the side by a pump. Although this pressure is limited only by the strength of the apparatus and frequently rises to 100 or even 150 lbs. per sq. in., the object of the operation may easily be defeated by using too great pressure, especially at the beginning. The size of the minute channels in the filtering cloth remains constant only when no part of the solid matter finds its way into these openings. If the precipitate to be filtered is crystalline and larger than the openings, a network soon forms on the surface of the cloth which protects the openings; but if the precipitate is gelatinous in nature, a large initial pressure can easily force enough of the solid matter into the channels to close them, and render filtration impossible.

Development of Filter Press.—If in the pressure filter just described, instead of the air-tight top there be fastened to the container a second false bottom and filter cloth exactly like the first, and the whole apparatus placed on its edge, the liquid mixture to be filtered may be pumped into the container as before and the clear filtrate will flow from *both sides*. The active filtering area is thus doubled at very small cost. When the container has become entirely filled with the solid, the mass may be easily and efficiently washed by fastening a shell, with an opening at the bottom, to each of the filtering faces, filling one shell with water through its opening, and forcing this wash water through the cake and out the other side. These shells will not interfere with the next operation of filtration, as the filtrate can discharge through the same openings as serve to introduce and discharge the wash water.

This pressure filter unit is now seen to consist of a chamber into which is pumped the mixture to be filtered, bounded on both sides by a filter cloth supported by a perforated structure or "false side." Next to each false side is a second chamber from which the filtrate passes from the filtering surfaces, and from one of which water may later be forced through the filter contents to the other.

It is obvious that a number of these units may be placed side by side on a common support, filled from the same pressure supply pipe, and discharge the filtrate into a common receiver. By placing these units close together, the space between the filtering faces will function as the shell above used for washing, so that by forcing water into every other such chamber, one becomes a supply space and each alternate chamber a discharge space for wash water.

If now the end filter be placed against a solid rigid support, and provision be made for firmly pressing the other filters against it, it is possible to omit the bolts which hold the false sides and filter cloths to the filter chamber, and hold the entire structure together by a heavy lateral pressure. In this way is built up an exceedingly important piece of apparatus known as the *Filter Press*.

It is apparent that an apparatus as above constructed may be much simplified. Instead of using a perforated plate as a support for the filter cloth, the plate may be solid, but supplied with checkered grooves or channels. The cloth is held against the face of this plate while the filtrate flows off through these channels. In another type the ridges radiate from the discharge opening which may be located either in the corner or center of the plate.

Filter-press Plates; Flush and Recessed.—If the ribbed portion of such a plate be recessed the cloth may be made to bulge into the hollow portion. When two plates of this type are placed together, a chamber for the solids is formed between the two

filter cloths, and the filter frame eliminated. These are known as "recessed plates" and when the amount of solids to be separated is small, and difficult to filter, such plates are to be recommended, as the cake when formed is thin and easy to wash. When the amount of solids is large, however, the plate should be flush, and the distance frames already described should be employed, as too great a strain on the filter cloth shortens its life. (See Fig. 85.)

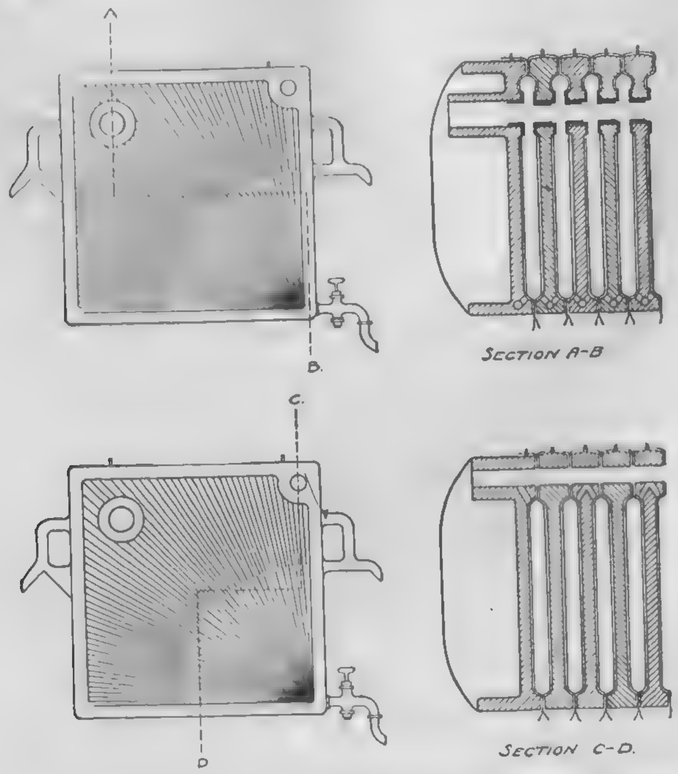


FIG. 84.—Diagram Showing Assembly of Recessed Rates.

Instead of supplying these filter frames from a pipe on the outside of the structure, each frame and plate may have a hole in the corner, thus providing a channel from one end of the press to the other. This channel may connect with the interior of each frame by an opening in the corner and through this channel the entire press may be fed. Figure 84 shows the two types of recessed plates which fit on either side of such a frame, the reverse side in each being the same. The upper is known as a "one-

button plate" and is provided with the discharge cock from the opening *B* to carry off the filtrate as it flows down the ribbed channels back of the filter cloth. The lower, called a "three-button" plate, has in addition at the upper right-hand corner, an opening for the admission of wash water to the recessed portion from the lateral channel *C*. When the frame is full of solids, the outlet cock of the "three-button" plate is closed, and water forced through this opening in behind the filter cloth. It

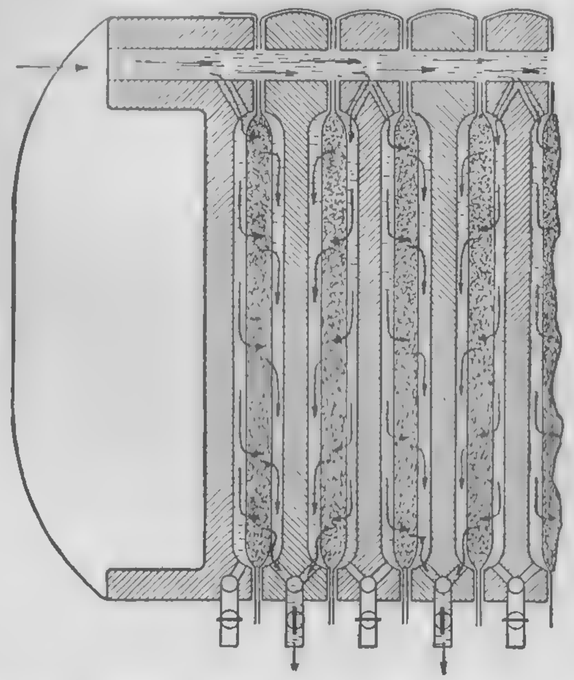


FIG. 84A.—Washing of Filter Cakes in Chamber Press with Recessed Plates.

spreads over the surface of this plate, passes through the cake and is collected on the face of the "one-button" plate and discharges through the outlet cock.

The two channels *A* and *C* must be provided with air-discharge cocks; when the mixture is first forced through *A*, the air in the frames and plates can escape through *C*; and when the wash water is supplied through *C* the air which would otherwise be trapped, escapes through *A*.[1]

Figure 84A shows the conditions during washing in a filter

[1] For a general discussion of filter plates, *see Chem. Met. Eng.*, **22**, 493.

press with recessed plates. The space between the filter cloth and the plate is much exaggerated to show the course of the wash water. Every alternate outlet cock is closed, the wash water being diverted into a separate run-off trough by turning the curved end on the outlet cock through 180°, or by means of a short piece of rubber hose on the end of the outlet cock. Obviously, the wash water must travel twice the distance through the press cake that the filtrate did. The end plates, supporting frames, and device for supplying the pressure to close the integral parts of the press must be of heavy construction and are generally of cast iron. The frames may be of iron, tin, zinc, lead-coated iron, bronze or wood, according to the properties of the material to be filtered.

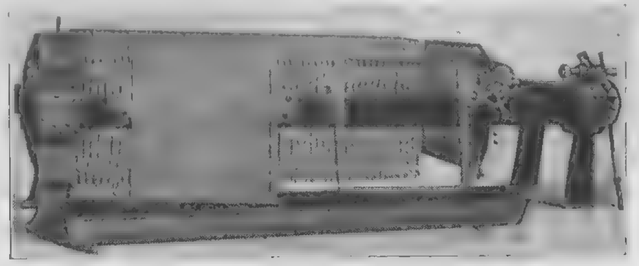


Fig. 85.—Shiver Plate and Frame (Chamber) Filter Press.

Presses may be constructed with channels in the frames and plates through which steam or cold brine can be circulated. In this way one can at will maintain the filtering surface at either a high or low temperature.

In order to empty a chamber press it is necessary to release the pressure on the plates and to separate the elements of the press by sliding each one along the supporting rods. The cloths are cleaned or replaced and the cakes are discharged into a hopper, or conveyor immediately below the press.

The filter press has a large area for its bulk, but washing, emptying and resetting are slow and labor charges high when compared to a leaf press. (See pp. 372 to 379.)

Leaf Filters.—Another method of supporting the filtering medium for either vacuum or positive pressure filtration is found in what is known as the "leaf" or the "submerged" filter. The principle may be understood by considering the filtering

mechanism shown in the diagram. A frame is made of heavy screen suspended from an outlet nipple, see Fig. 86, and enclosed in heavy filter cloth. When this leaf is submerged in the liquid magma and a vacuum applied to the outlet pipe, the liquid is drawn through the cloth, while the solids adhere to the outside of the leaf. In addition to the diminished pressure maintained within the filter leaf, a positive pressure may be exerted upon the liquid mass in which the leaf is submerged. When a layer of sufficient thickness, which varies from $\frac{1}{4}$ to $1\frac{1}{2}$ in., has been obtained it may be washed in two ways. The loaded leaf with the vacuum still on may be transferred to a second vessel filled with water, and enough water drawn through to wash the precipitate, or, the magma may be withdrawn from the first vessel and replaced with water without moving the leaf. The charge of solids adhering to the leaf may now be quickly discharged by forcing air or water through the leaf in the reverse direction; it is then again ready to be immersed in the filtration tank.

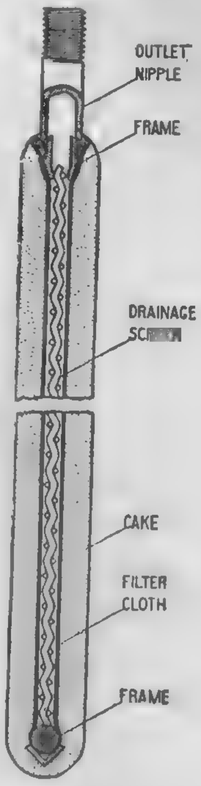


Fig. 86.—Moore Filter-leaf.

This idea has been utilized in a number of forms, the more important at present being that of the originator of the method, the Moore, and, those for positive pressure, the Kelly and the Sweetland presses.

Moore.—The first of these is simple in construction, though it does not so easily admit of applying a positive pressure to the outside of the filtering leaf. The leaves are constructed in multiple in frames carrying 30 or more, and the whole lifted and transported by a crane. In operation the frame is lowered into a tank containing the material to be filtered, kept continuously agitated. When suction is applied to the outlet pipe, the liquid passes through the cloth and the precipitate builds up an adhering cake. The cake is washed by bodily lifting the frame, suction being maintained, and immersing it in a tank of water or dilute wash water. It is dried more or less by suction and discharged by blowing water, air or steam back through the leaves.

Kelly.—The Kelly press consists in a heavy supporting frame upon which is mounted a pressure tank or press shell, which holds the material to be filtered when under pressure; a traveling filter carriage supporting the filter frames, each made up as already described of a frame and a filter cloth covering, the whole telescoping into the tank; a closing device, forming the head of the pressure tank by means of which the filter frame and leaves are

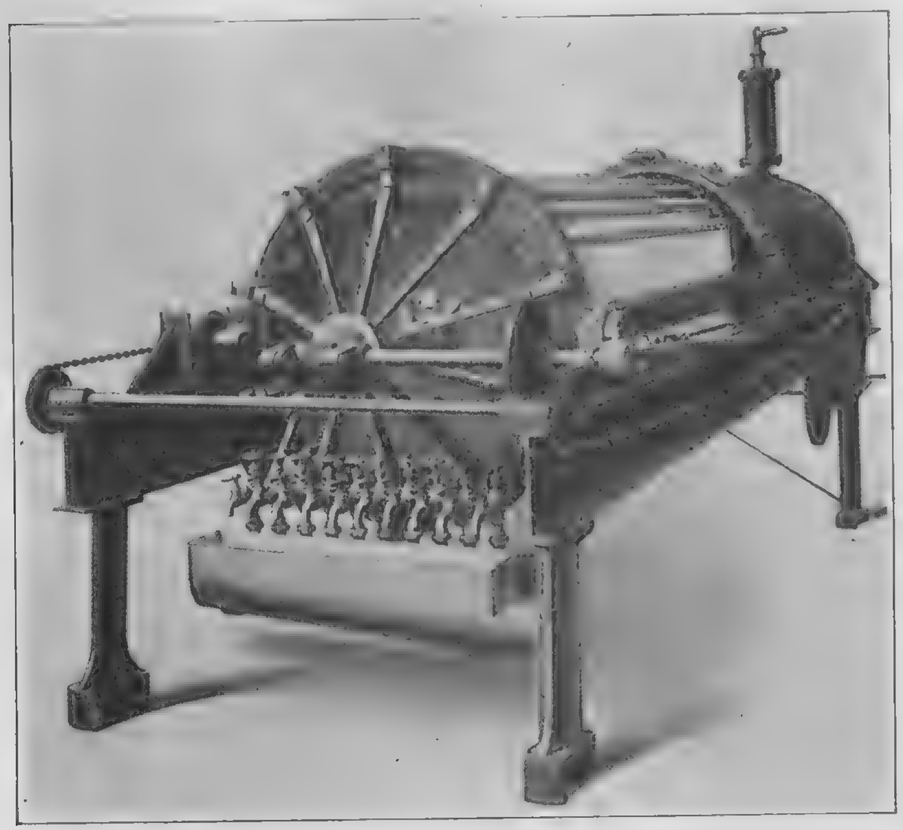


FIG. 87.—Kelly Filter Press.

tightly locked within the tank, and a series of automatic air and water valves.

Each leaf on the carriage is connected to a discharge cock in the head, and is proportioned in size to conform to the circular cross-section of the pressure chamber into which it runs. The operation of the filter is as follows: the carriage is drawn into the chamber, locked, and the liquid mixture forced in. The air

escapes through a valve and the clear filtrate flows from the cocks in the head to the discharge gutter. Should any leaf fail to give a satisfactory filtrate it may be cut off by closing the cock as in the old type of filter press.

In case there is a tendency for the heavy particles to settle to the bottom of the tank before they become attached to a filter leaf, a circulation of the mass may be maintained by allowing a little liquid to flow back to the feed tank. The thickness of the cake is automatically determined by a tell-tale device.

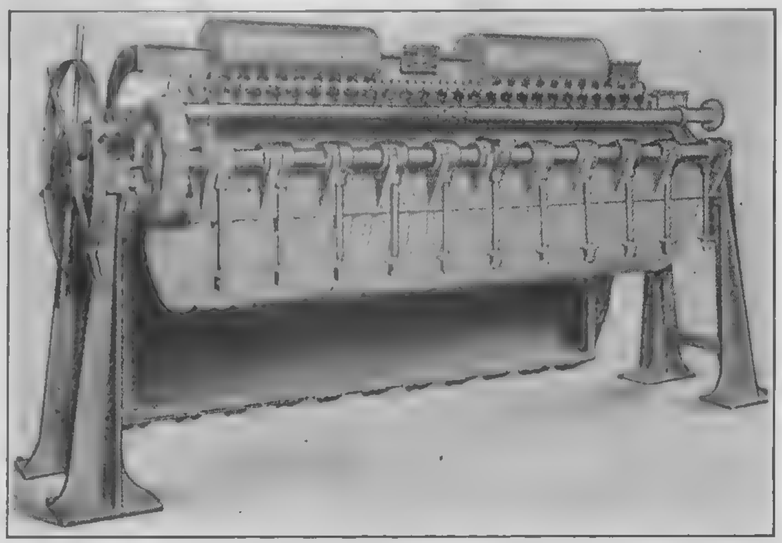


FIG. 88.—Sweetland Filter Press.

As soon as cakes of sufficient thickness have been formed, the excess liquid is drained off, or forced out of the tank by means of compressed air, and wash water is forced in. When washing is completed, the head is unlocked and the carriage and loaded leaves run out of the tank by gravity. Compressed air, steam or water is now forced into the leaves and the adhering cakes are blown off; when the cakes are removed the counterpoise weights draw the carriage back into the tank, and the cycle is repeated.

Sweetland.—The Sweetland press consists of two semi-cylindrical castings, the upper half being held rigid in its support and carrying circular filter leaves with suitable outlet connections. The lower half is hinged to the upper, and is capable of closing

upon it, forming a tight pressure chamber, and later swinging open, exposing the leaves.

The operation of the press is in principle the same as the Kelly press, suitable provision being made for supplying and withdrawing the liquid magma and wash water and the compressed air for discharging the filter cake from the leaves. Some types provide for spraying the leaves with wash water while the shell is empty instead of entirely filling the shell with water, and for using a

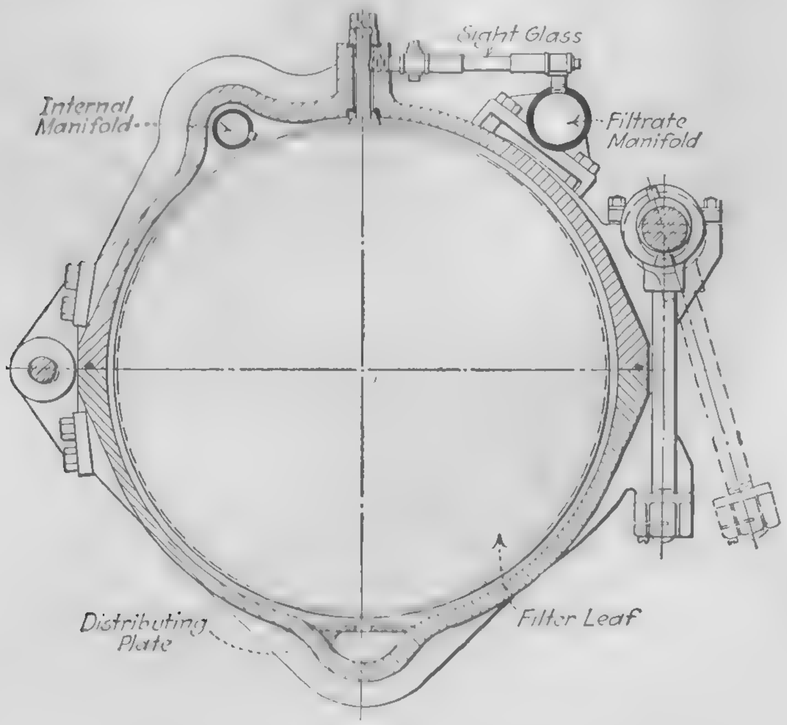


FIG. 89.—Cross-section of Sweetland Press.

stronger spray, directed against the leaves, for sluicing out the sludge without the necessity of opening the press.

Filters of the foregoing type have been on the market for relatively few years, but the principle is capable of being utilized in many cases and greatly modified to suit individual conditions.

Continuous Rotary Filters.—The suction filters already described are stationary flat surfaces on which the precipitate is drawn by suction, and from which the accumulated sludge is

periodically removed, either by scraping or by internal pressure. By making the filtering surface take the form of a rotating drum, from the hollow trunions of which the filtrate is continuously removed, a new type of filter now much used for free filtering

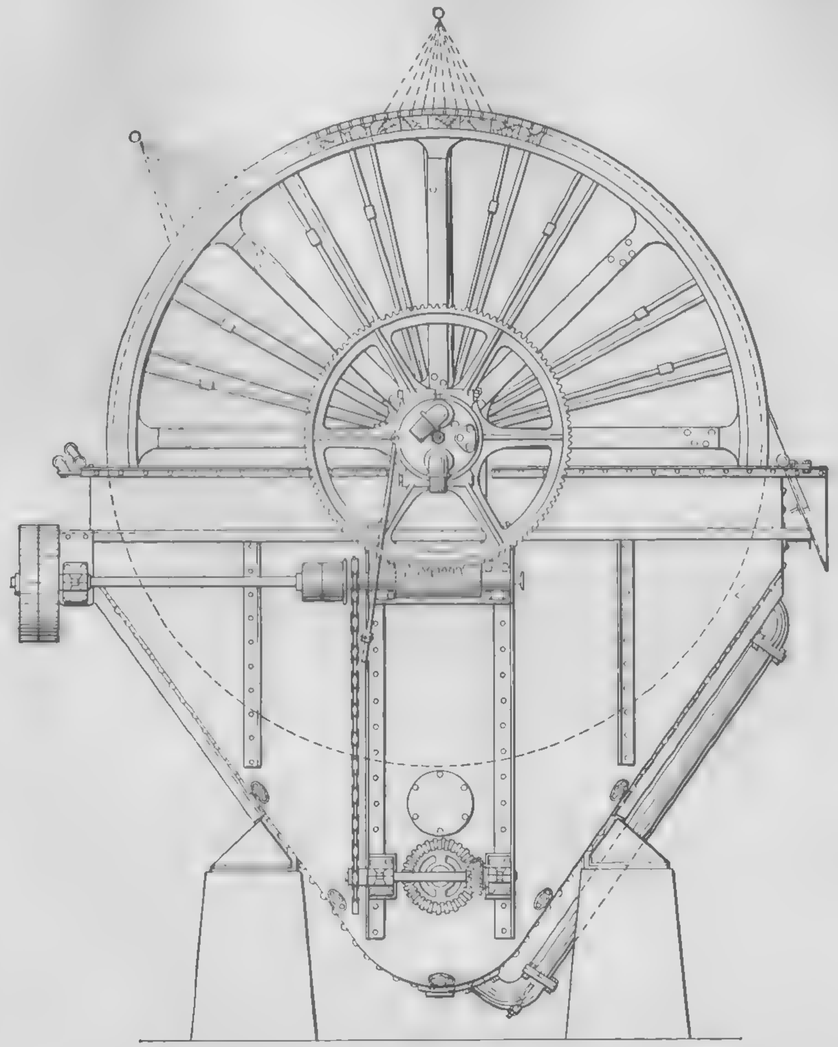


FIG. 90.—End View of Oliver Continuous Rotary Filter.

solids such, for example, as precipitated calcium carbonate, is obtained.

The rotating element may be either a disk or a drum, the surface of which is made up of a number of shallow compartments

over which is placed the filtering medium. If a disk, these compartments are segments of the circle forming the sides; if a drum, they are portions of the peripheral area. In either case these compartments are connected to the shaft by separate pipe systems leading to ports in the hub. The rotating portion is immersed in a tank of the material to be filtered. Those compartments which are submerged are at this time connected to the suction ports of the hub, the filtrate is drawn through the hollow trunnion and the sludge is deposited on the filter. When a compartment emerges from the liquid, the port connecting with the filtrate suction closes, and one connecting with the wash water suction opens. Wash water is sprayed at considerable pressure on the surface of the deposited sludge. When sucked reasonably dry, a third set of ports is reached, and compressed air, water or steam is blown through in a reverse direction, and the filter cake is blown off into a suitable receptacle.

Filters of this type require little labor, and are adapted to free filtering materials in solutions at a temperature such that vapor pressure does not defeat the action of the vacuum pump.

Bag Filters.—Bag filters are a type using the principle of hydrostatic head. They are made of twilled cotton, always supported by coarse netting strong enough to stand the pressure used. When hot liquids are filtered the bags may be hung in a steam-heated room where the temperature can be maintained as high as desired. This type of filter is being rapidly replaced by the mechanically operated ones.

Centrifugals.—Centrifugal force may be applied to the separation of solids from liquids with great advantage providing the nature of the solids is such that they do not under pressure form an impervious or impenetrable layer. Hence for the separation of liquid from cotton, wool, or fibrous material of any kind or from granular or coarsely crystalline substances the so-called hydro-extractor or centrifuge is extremely serviceable. Although there are a number of types of such machines the principle of all is the same, namely, the rapid rotation of a perforated cage or basket in which the material is placed and which retains the solids while the liquid portion is pressed through into the outside casing. The revolving element must be free to assume as a center of gyration the center of gravity of the basket and its load. Therefore provision must be made for allowing the basket and

supporting shaft upon starting to swing somewhat from the perpendicular.

Hydro-extractors may be over-driven, that is, suspended and driven from a rigid support over the basket, or they may be under-driven as in Fig. 91. They are made of many materials such as steel, bronze, stoneware, etc., and the perforated basket is covered with such filtering medium as best serves the purpose at hand. For many materials the basket itself suffices.

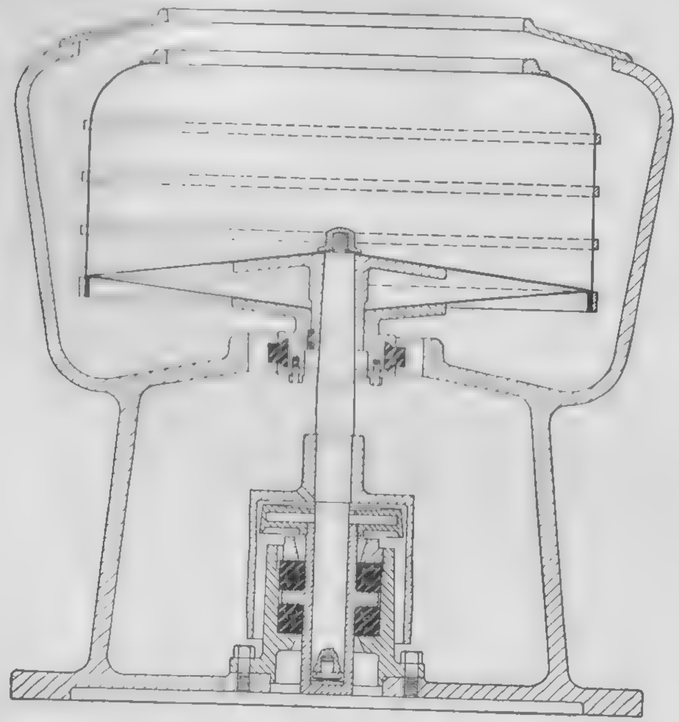


FIG. 91.—Hydro-Extractor.

In textile work hydro-extractors are best discharged by lifting the load out through the top of the basket. For the chemical industries extractors may be built with a removable bottom which allows the charge to be dropped into a chute or conveyor.

When atmospheric or hydrostatic pressures are employed in filtration, suitable gauges are available for determining both the safe and efficient working conditions. There is, however, no ready means for finding the pressure being exerted upon the charge or the basket in a hydro-extractor, so that recourse must

be had to a calculation of the pressure due to the centrifugal force which obtains when the apparatus has reached its working speed. The formula for centrifugal force is

$$F=\frac{WV^2}{gR}=\frac{W(2\pi RN)^2}{gR3600}=0.000341WRN^2,$$

where W is the weight in lbs., R the radius in ft., and N the r.p.m. This is the radial component of force and therefore the measure of the tendency of the liquid to leave the solid.

(3) Filters with Rigid Porous Membrane

When ordinary brick or pottery clay is burned at a low temperature a rigid material is produced which is filled with a large number of very small channels. It is clear that the plastic mass may be given any desired shape before burning and that the porosity may be controlled by the density of the plastic structure. For some purposes such a material furnishes an excellent filtering medium. A filter may be constructed by fitting tiles or blocks of this material as a lining to any convenient container and drawing away the filtrate from below. A pressure filter, much like the leaf type in principle, may be made from a series of porous cylinders with one end closed and the other set in a head piece, the whole being enclosed in a container which holds the liquor to be filtered. Between the cylinders is placed a mass of coarse sand under which are ports for compressed air. When the cylinders become clogged air is blown up through these ports and the sharp sand effectively scours the filtering membrane and removes the accumulated sediment. Filters of this type are efficient in removing exceedingly small particles and are much used in purifying water for domestic use.

In recent years a natural, porous, silicious material (Filtros) has been introduced for such filter construction. It can be cut into blocks and cemented into place. It is acid resistant and has proven very successful for filters of this type.

(4) Filters with a Semi-Permeable Membrane

The property possessed by some substances of passing in solution through a membrane such as animal bladder or parchmentized paper which holds back other dissolved substances,

furnishes a method of separation sometimes of great value. This is known as *dialysis* and is extensively used in the beet-sugar industry. The dialysing apparatus for extracting the soluble "crystalloid" from the liquor is built up much like a filter press. The liquor and water are introduced slowly through two funnels and pass through alternate chambers which are separated by parchment. The crystalloid diffuses through the membrane into the water and the two liquors are drawn off continuously through separate pipes.

Separation in Hydraulic or Screw Presses

When it is necessary to remove a small amount of liquid from a relatively large amount of solid, as for example, the contained oil from seeds or the adhering oil from paraffin wax, a much greater pressure is required than can be exerted in the filter presses already considered, and a screw or hydraulic press is used. This is a very strongly built frame between the ends of which the mass, enclosed in properly designed receptacles, is placed and subjected to a great pressure either by a powerful screw acting through a toggle joint or by a hydraulic ram.

Pulpy materials, *e.g.*, apples for cider, are effectively handled in a press [1] consisting of a truncated conical shell built up of steel bars closely set together and fitted with a powerful internal screw. The stock is fed from a hopper at the larger end and forced through the shell parallel to its axis by the screw. The liquid exudes through the small cracks between the bars. The pressure is regulated by controlling the size of the outlet at the small end of the press and the time of exposure of the stock to pressure depends on the rate of rotation of the screw. The liquid must travel a relatively long distance through the stock and the pressure is not so high as in a hydraulic press but the capacity is very large and the labor costs negligible and, where applicable, this type is unexcelled.

NOTES ON OPERATION OF FILTERS

Back Pressure Operation.—In pressure filters with a closed delivery system, the drop in pressure from one side of the filtering medium sometimes results in conditions making continuous

[1] See Fig. 108, p. 484.

operation difficult. Thus, for example, hot liquors become supersaturated owing to the very rapid evaporation due to fall in pressure; the acid carbonates of calcium and magnesium lose their carbon dioxide and separate a crystalline deposit in the cloth. This trouble may frequently be eliminated by maintaining the discharge under a positive pressure until free from the press. This may easily be done by passing the filtrate from the press or plates through an inverted U-pipe open at the top and discharging at the press in full view of the operator. To be sure this pressure acts against the pressure on the pump side of the press; but this loss can easily be made up by increasing the working pressure of the pump by this amount, since the effective pressure is the difference between that obtained inside the leaves or plates and that on the outside.

Choice of Pump.—For many years pressure filtration was limited to reciprocating pumps and compressed air in a monte jus. The former is frequently objectionable on account of the pulsations of the stroke unduly compressing the cake, and the tendency, even when supplied with ball valves, to fail to function due to grit or other material wedging the valves. The monte jus is ideal from many points of view, but is cumbersome and consumes much compressed air. Centrifugal pumps are efficient if the size is adapted to the discharge rate. If too large, and the rotor becomes an agitator, good filtration is sometimes made very difficult. The rotary displacement pumps are rightly becoming very popular, because they combine positive action with an absence of valves and pulsations. Provision must be made for by-passing the discharge back to the supply tank when the working capacity of the press is exceeded.

Uniformity of Cake.—Where it is desired to wash a cake, especially in leaf filters, it is imperative to have it uniform in order to get equal distribution of wash water. If the sludge particles are non-homogeneous in size and shape, *e.g.*, where "filter-aid"[1] has been added, the slurry must be kept agitated during filtration. Otherwise the heavy particles will settle out and accumulate on the bottom of the leaf while the finer particles which filter less freely will be at the top. In such case the bottom will wash well and the top not so well.

When a sludge settles at an appreciable rate, decantation

[1] See p. 342.

should precede filtration, even though it be necessary to pass the turbid liquid through the filter. This generally prevents the sludge from settling in the filter, although with non-homogeneous sludges, or those containing filter-aids, agitation may be necessary to insure an even filter cake.

Life of Filter Cloths.—If the liquids filtered are either acid or alkaline in reaction it is very important to avoid concentration upon the filter cloths due to drying out of the cloth either during the dumping and cleaning period or while the press is not in use. Otherwise serious deterioration of the cloth will result. When not in use, the press should be kept filled with water not only to protect the cloths but also because any corrosion will form non-adherent oxide which can be readily removed prior to use.

Plugging of Cloths.—Especially in the case of fine, slimy precipitates the sludge is likely to force its way into the fabric and plug up the finer openings of the cloth, resulting in marked increase in resistance. In many industries the commercial life of filter cloth is limited by this plugging effect rather than by weakening of the fabric. Sometimes the material can be removed by a suitable solvent, but often it is very refractory. Where allowable it is desirable to minimize this effect by first charging the press with "filter-aid" to form a removable filtering medium which will prevent the finer precipitate from reaching the cloth. Wire fabric has less tendency than cloth to plug up in this way and will stand more drastic treatment in cleaning.

Choice of Filters.—When a new problem in filtration comes up it is impossible to predict with assurance what one of the many factors influencing the choice of filter equipment will be controlling in importance, but the following generalizations may be helpful.

The positive pressure type of leaf filter is used to handle sludges which filter with difficulty and therefore require pressure. With it the sludge may be subjected to a long, thorough washing. Furthermore the solutions and wash water can be hot, even above the boiling point at atmospheric pressure, without evaporation or serious cooling during filtration. Since they are readily cleaned they are especially adapted to the handling of extremely large quantities of sludge.

In the chamber press high pressure and temperature may also be used without difficulty. Washing, however, is less efficient

than in leaf filters because reversal of flow through the half-cake opens up channels. The labor cost of dumping and reassembling is much greater than in the leaf press, but the initial cost per sq. ft. of filtering area is less. Consequently the chamber press is superior to the leaf where the ratio of sludge to liquor handled is small and especially where it is unnecessary to clean the press frequently. For small scale operation it usually is superior to other types. It can also be made to give a dry, hard cake.

Free-filtering materials which can be filtered cold and which require no washing, or at most a short washing period, are best handled on the continuous rotary type of filter. For purely de-watering operations these are extremely successful. The scale of production must be reasonably large to justify their installation.

For the removal of very small amounts of precipitate from large volumes of water, sand filters are frequently employed. The removal in this case is to no small degree a matter of entanglement of the precipitate on the surface of the filtering medium. This type is extensively used in water purification. Box filters with cloth or other filtering medium are occasionally employed for small scale work, especially for very free-filtering solids.

Acid liquors can be handled in plate and frame presses constructed of wood, on acid-proof continuous rotaries or in open-tank vacuum-leaf filters of wood or lead. Alkaline liquors are successfully filtered upon a medium of woven wire cloth or screen.

De-watering of very free-filtering solids (crystals) is best carried out in centrifugals. In such apparatus the solution on the surface of crystals which are not too fine (30 or 40 mesh) can be reduced to below 5 per cent.

FILTER CALCULATIONS

A filter cake consists of a mass of small particles, irregular in shape, closely packed together. The liquid passing through the cake flows through the voids between these particles, and always follows straight line motion.[1] The cake may be considered as equivalent to a series of capillary tubes of definite average diameter. The flow through any one of these equivalent capil-

[1] See p. 73.

laries is given by Poiseuille's equation,

$$P = \frac{32\mu L u}{gD^2},$$

where P = the pressure drop, μ the absolute viscosity of the liquid, L the length of tube, u the linear velocity of the liquid, and D the diameter of the capillary. For a filter cake of thickness L and area A, with K capillaries per unit area,

$$\frac{dV}{d\theta} = K\frac{\pi D^4 P g A}{128\mu L},$$

$\frac{dV}{d\theta}$ being the rate of flow in volume per unit time.

This equation cannot be applied directly to the solution of filtration problems, but an understanding of it helps to explain the phenomena encountered and to develop a workable equation.

This equation indicates that for incompressible sludges, *i.e.*, those with constant size of voids, the filtration rate is proportional to the pressure, but that for compressible sludges the filtration rate will increase much less rapidly than in proportion to the pressure because the increased pressure decreases the size of opening. That the behavior of sludges under pressure will vary greatly with the character of the sludge may therefore be expected.

Since the rate of flow through capillary tubes is inversely proportional to the viscosity of the fluid, filtration is retarded by decreasing the temperature because of the increased viscosity of the liquid to be filtered. The available data are insufficient to prove exactly what relationship exists. Where the physical character of the sludge does not change with temperature, it may be assumed that the rate of flow is inversely proportional to the viscosity, a relationship indicated by the experimental results on homogeneous incompressible sludges.

The equation also indicates that the filtration rate is directly proportional to the area of the filter and inversely proportional to the thickness of the cake.

Differential Equations for Incompressible, Homogeneous Sludges

Since the pressure drop through a cake is proportional to the velocity of flow, it is most convenient to consider filtration rate

as equal to the driving force, *i.e.*, the pressure, divided by the resistance. This resistance consists, however, of two parts, the resistance of the cake itself, R, and that of the press and filtering medium. In a well-designed press the resistance of the main channels should be negligible, whence the press resistance will be inversely proportional to the filtering area. It is therefore assumed as such. Hence

$$\frac{dV}{d\theta} = \frac{P_t}{R + \frac{\rho}{A}} \quad \ldots\ldots\ldots (1)$$

The meaning of all symbols is given in the Nomenclature Table, p. 363. For those cases in which the resistance of press and filtering medium is small compared with that of the cake (as is usually true for slow-filtering sludges) this simplifies to

$$\frac{dV}{d\theta} = \frac{P}{R} \quad \ldots\ldots\ldots (1a)$$

For the time being this form will be used and the correction term for press resistance inserted later. Since resistance is proportional directly to the length and inversely to the area of a conductor, obviously $R = \frac{rL}{A}$. Also, since the volume of the cakes in the press is LA, while the sludge brought in by the liquor is vV, equating these gives

$$L = \frac{vV}{A}.$$

Thus one may write

$$R = \frac{rvV}{A^2},$$

whence the Eq. (1a) becomes,

$$\frac{dV}{d\theta} = \frac{PA^2}{rvV}, \quad \ldots\ldots\ldots (2a)$$

or, allowing for the press resistance, Eq. (1) becomes,

$$\frac{dV}{d\theta} = \frac{P_t A^2}{rvV + \rho A}. \quad \ldots\ldots\ldots (2b)$$

Nomenclature

A = total area of filtering surface in sq. ft.
V = total volume of filtrate in cu. ft. obtained up to the variable time θ.
v = volume of cake, as it collects on the filter, in cu. ft. per unit volume of filtrate.
P = pressure drop through the cake.
P_t = pressure drop through cake, filtering medium, and press channels.
θ = total time of operation.
R = total resistance of the cake to flow of filtrate through it.
r = specific resistance of the cake, *i.e.*, the resistance of a unit cube.
r' = coefficient in the equation: $r = r'P^s$.
r'' = coefficient in the equation: $r = r''P^s(dV/Ad\theta)^t$.
$\frac{\rho}{A}$ = resistance of the press channels and filtering medium, where ρ is a coefficient.
L = thickness of cake at the variable time θ.
s = coefficient of compressibility = zero for non-compressible sludges but in no case greater than unity even for the most compressible ones.
t = coefficient of velocity effect (scouring) = zero for homogeneous sludges but seldom over 4 or 5.

Equation (2a) or (2b) is entirely satisfactory for incompressible sludges, *i.e.*, for those in which increase in the pressure on the press will not decrease the equivalent diameter of the voids between the particles. Actually it is doubtful if such sludges exist in commercial practice. It is possible to produce such a sludge artificially by taking a material, like kieselguhr, packing it into a press, subjecting it to high pressure and then operating at a pressure always lower than the maximum to which it has already been subjected. Under such conditions this equation holds quantitatively. However, this equation, although not exact, is satisfactory as an engineering approximation for sludges made up of sand, calcium carbonate, sodium bicarbonate or other coarse, granular, strong particles.

Differential Equations for Compressible, Homogeneous Sludges

However, most sludges are distinctly compressible. For example, very fine particles, such as barium sulphate, although undoubtedly granular, are capable of being packed more closely under high pressure and the increased velocity of flow around the particles which results therefrom. Hydrated sludges, such as

the heavy metal hydrates, the calcium phosphate used for defecation of sugar syrups and the like, are highly compressible and the specific resistance increases enormously with increase of pressure. For such sludges the general use of this equation in the form given in Eq. (2*a*) or (2*b*) is not permissible.

While a great deal of experimental work has been done in this field, the theoretical solution of the problem is extremely difficult and has not been accomplished. In the first place, sludges which show the effect of compressibility to a high degree are hydrated precipitates, the degree of hydration and particle size of which are extremely sensitive to the conditions under which the precipitates are produced and change progressively with time. Consequently the production for experimental work of sludges of fixed characteristics is very difficult. Furthermore the properties of these sludges are so exceedingly sensitive to temperature that slight temperature changes during filtration seriously affect the results. Despite these experimental difficulties in checking quantitatively theoretical conclusions, it can be definitely stated that, for the practical problems of engineering design, it is sufficient to assume that the specific resistance, r, is a power function of the pressure, the exponent, s, being less than unity. Consequently $r = r'P^s$, whence

$$\frac{dV}{d\theta} = \frac{PA^2}{r'vVP^s} = \frac{P^{1-s}A^2}{r'vV}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Differential Equations for Compressible, Non-Homogeneous Sludges (General Case)

Since it is these slimy, compressible precipitates which offer the greatest filtration resistance and are most difficult to handle, much effort has been expended in improving the methods of filtering them. One of the most successful devices developed is the addition to these precipitates of a certain amount of porous, granular material to open up the mass and make filtration easy. Of these so-called "filter-aids" diatomaceous earth is one of the best. In the filtration of such sludges with the addition of "filter-aids" it is found that a *constant rate* of filtration with increasing pressure is on the average much more rapid than a constant pressure filtration in which the pressure is maintained throughout the run at the maximum value realized at constant

rate. The major reason for this is apparently as follows: If at the start of a filtration high pressure be used, the initial velocity is extremely high because the thickness of the cake and therefore its resistance is small. This high liquor velocity tears off the slime which is adhering to the particles of filter-aid, *e.g.*, the diatomaceous earth, brings it again into suspension in the liquid, and forces it forward through the cake. It finally reaches a crevice in the cake through which the precipitate cannot pass, but all such crevices are soon plugged up and there develops during the initial stages of filtration an excessively high resistance in the cake. Since this sludge first laid down remains throughout the filtration cycle, the average rate of filtration is correspondingly reduced. If, on the other hand, the filtration is started at a moderate rate which will not scour the slime off the filter-aid, the resistance does not develop in this way and the effective filtering rate is increased. This phenomenon is encountered not only where filter-aids are added, but also in those cases where the precipitate itself consists of particles of diverse size, the larger lumps of which are granular and relatively strong, as in the case of filtering carbon from pitch and the like.

Apparently this phenomenon of scouring does not develop in homogeneous precipitates, however compressible. Homogeneous compressible precipitates will, however, under certain conditions filter faster on the average at constant rate than at constant pressure; but when this occurs examination of the cake before filtration is completed will show evidence of sedimentation, *i.e.*, the filter has been used as an apparatus for decantation. In general a sludge should be decanted as far as possible prior to filtration because construction and operation of decantation apparatus is cheaper than that of filters. In other words, where the filters are laid out and operated to the best advantage decantation will not occur in the filter to an appreciable extent and Eq. (3) will apply.

In the case of the mixed precipitates this scouring effect may be estimated by assuming the increase in coefficient of resistivity as proportional not only to P^s, but also to a power function of the linear velocity of the filtrate through the cake, the exponent being t, *i.e.*, $r = r''P^s\left(\frac{dV}{Ad\theta}\right)^t$. Since if plugging due to scouring once occurs in a cake no later reduction in velocity or pressure will

reduce the resistance already developed, this velocity term must be an integrated effect, but this does not apply to the pressure term, which may be taken outside the integral sign. Obviously, $dR=rdL/A$ and, since $dL=vdV/A$,

$$R=\frac{r''vP^s}{A^{2+t}}\int\left(\frac{dV}{d\theta}\right)^t dV.$$

The general filtration formula therefore becomes

$$\frac{dV}{d\theta}=\frac{P^{1-s}A^{2+t}}{r''v\int(dV/d\theta)^t dV} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For homogeneous sludges, $t=0$, and (4) reduces to (3).

Integrated Equations

Integration of these expressions gives the following equations. In all cases it is assumed that $V=0$ at $\theta=0$.

Homogeneous Sludges

Constant Pressure:

$$\frac{V^2}{A^2}=\frac{2P^{1-s}\theta}{r'v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

Constant Rate:

$$\frac{dV}{d\theta}=\frac{V}{\theta}=\text{const.}=\frac{P^{1-s}A^2}{r'vV} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

Constant Pressure Gradient through cake:

$$\left(\frac{P}{V}\right)^{1-s}=\text{const.}=\frac{r'vV^{1+s}}{A^2\theta(1+s)} \quad . \quad . \quad . \quad . \quad . \quad (3c)$$

Sludges with Filter-aids or Equivalent

Constant Pressure:

$$\left(\frac{V}{A}\right)^{2+t}=\frac{P^{1-s}}{r''(1+t)v}\left(\frac{2+t}{1+t}\theta\right)^{1+t} \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Constant Rate:

$$\frac{dV}{d\theta}=\frac{V}{\theta}=\text{const.}=\left(\frac{P^{1-s}A^{2+t}}{r''vV}\right)^{\frac{1}{1+t}} \quad . \quad . \quad . \quad . \quad (4b)$$

The last two equations are less certain than the first three but are satisfactory for purposes of interpolation.

Equations for Box Filters

Box filters are usually operated under static head only. Quantitative discussion therefore requires certain modifications of the general equations. Details of cases which frequently arise are given below.

Special Case A. Very Slight Precipitate.—Filters used for the removal of small precipitates offer no resistance to filtration other than the resistance of the filtering medium itself. The filtering medium may be cloth, paper, sand, coke or gravel, and the rate of flow through the voids between the solid particles of the filter follows the laws of viscous motion (p. 73). The cake obtained on filters of this type is negligible.

Assume the temperature of filtration constant and therefore the viscosity unchanged. The pressure is exerted by means of the hydrostatic head of liquid, H.

Therefore,

$$\frac{dV}{d\theta}=KHA, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or integrating, assuming H is maintained constant,

$$V=KHA\theta+\text{constant.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

This constant of integration equals zero if time and volume of filtrate be taken as zero simultaneously.

If, however, the box filter be filled at the start and allowed to drain at constant temperature without the addition of any more liquid in the meantime, the rate of flow will at all times be proportional to the area of the box and the head prevailing at the time. Assuming that the box has straight sides and therefore A is constant,

$$\frac{dV}{d\theta}=KAH,$$

or substituting $-AdH$ for dV and integrating between the limits H_1 and H_2,

$$ln\frac{H_1}{H_2}=K\theta.$$

The head H should be measured to the bottom of the bed. Since these equations are calculated for a constant thickness of filtering medium, they do not hold where the liquor level falls below the surface of the bed.

Special Case B. Granular Precipitates which Settle Readily in Box Filter.—For granular precipitates, which may be considered incompressible, the rate of flow is directly proportional to the pressure. A highly granular precipitate will settle to the bottom of the box almost immediately and therefore with a constant head, the thickness of the cake is directly proportional to the

volume added to the filter plus the initial thickness, *i.e.*, the thickness of sludge which entered with the liquid necessary to fill the box, or

$$L = L_0 + \frac{\alpha V}{A},$$

where L_0 = the initial thickness of the sludge.

$$\frac{dV}{d\theta} = \frac{KHA}{L} = \frac{KHA}{L_0 + \frac{\alpha V}{A}}, \quad \ldots\ldots\ldots \quad (6)$$

$$\frac{L_0 dV}{A} + \frac{\alpha V dV}{A^2} = KH d\theta, \quad \ldots\ldots\ldots \quad (6a)$$

$$\frac{L_0 V}{A} + \frac{\alpha V^2}{2A^2} = KH\theta + \text{constant}. \quad \ldots\ldots \quad (6b)$$

For varying heads, *i.e.*, in case the filter is filled and then allowed to drain without adding any further liquid, this case simplifies to the preceding one, and as before,

$$ln\frac{H_1}{H_2} = K\theta. \quad \ldots\ldots\ldots \quad (6c)$$

This is because the precipitate settles at the start of the filtration and being incompressible, the sludge simply acts as a sand filter of type A.

Granular precipitates which settle easily but are compressible obey the same laws, because if the head is constant, the precipitate is compressed equally throughout the filtration; and if the head is allowed to fall, the greatest pressure is at the start and a precipitate once compressed under not too high pressure does not greatly alter in compactness by diminishing pressure. This compression can be allowed for in the equation, for since

$$L = kH_1,$$

$$\frac{dV}{d\theta} = \frac{KHA}{kH_1}.$$

Then when the head falls and $dV = -AdH$,

$$ln\frac{H_1}{H_2} = \frac{c\theta}{H_1}. \quad \ldots\ldots\ldots \quad (6d)$$

NOTES ON USE AND INTERPRETATION OF EQUATIONS

The equations for filtration under constant pressure check the experimental data within its precision, *i.e.*, during a given run the ratio V/A is proportional to the square root of the time (see p. 366) and the proportionality constant varies from run to run

as a power function of the pressure, the exponent being $1-s$. The exponent s varies from 0 in the case of incompressible sludges to a maximum of approximately 0.85 for the most compressible ones. On the other hand the constant rate equations for compressible sludges do not hold during the early stages of filtration. At the start of the filtration cycle at constant rate, the pressure builds up quite suddenly to a value far higher than the equation would indicate. It then remains almost constant for a period but finally flattens off to substantial agreement with the equation. It seems likely that this discrepancy in the early stages of the run is caused by plugging of the filter cloth. The phenomenon develops in marked degree only in the case of highly compressible sludges, the cake resistance of which at low pressures is negligible compared with that at high. When such sludges are forced into the voids of the filtering medium they are packed into a net filtering area far below that corresponding to the term "A" of the equation, which represents the gross area of the filter. This plugging resistance developed is therefore very large compared with that indicated by the equation for the early stages of the run. It is, however, negligible in its effect when the whole filtering period is considered. Since in engineering design one has relatively little interest in the early stages of the cycle, the equations for constant rate can be employed with safety because they correspond with the overall performance of the apparatus. This plugging effect is not detectable in constant pressure runs because in such the resistance of the early layers of sludge laid down is high compared with this correction term.

General Applicability.—In the case of homogeneous, compressible precipitates filtered under conditions such that decantation does not play a part in the filtering operation, while the coefficients, s and r', determined thus from constant pressure or constant rate conditions check reasonably well, the value of r' at constant rate seems to be higher than that obtained at constant pressure. Where decantation takes place in a filter with vertical filtering surface it is a great deal lower. In consequence one should always experimentally determine these coefficients on the particular sludge for which the equation is to be employed under conditions as nearly similar as may be to those of actual operation; *i.e.*, if one proposes to operate at constant pressure or constant rate or constant pressure gradient, the experimental data should be obtained on this

particular type of cycle. On the other hand, given data obtained under one set of conditions, the equation may be safely used to secure a preliminary estimate of the influence of change in those conditions.

Variability of Individual Sludges.—As has already been indicated, *compressible* sludges are extremely sensitive to the conditions under which they are produced and rapidly change in character with time, although this change usually becomes progressively less the longer this period. Data have been obtained on sludges produced and filtered under supposedly identical conditions, the filtering time of which varied four-fold. Because of this sensitiveness, laboratory data obtained from small-scale experimentation cannot be used with safety for purposes of engineering design except as a first approximation. It is possible in the laboratory to produce the precipitate in question under conditions which will yield a sludge of maximum specific resistance so that equipment based on such data will at least be safe. It is, however, impossible to estimate the magnitude of the factor of safety thus introduced. Consequently where equipment is to be installed for a new process, on the basis of small scale experimentation only, it should be designed on a reasonable basis, but with provision for expansion should this prove necessary.

Constancy of Operating Averages.—For one important purpose these equations are entirely dependable. Where a plant is in normal operation, the constants of these equations can be obtained from the *average* performance of the filtration equipment used on the sludge produced under normal conditions. Such constants obtained from average plant performance can be used with safety to estimate the result of proposed modification in operating conditions in the plant or for the design of filters for new installation provided the precipitate in the new plant is to be produced under conditions identical with those in the old one. (See problem on p. 379.)

Washing.—While data on filtration can be used to secure an estimate on washing time it is safer to obtain washing data directly, especially in the case of chamber or " plate and frame " type of filters, because in these the half-cake through which flow is reversed on washing is loosened up by this reversal and its resistance lessened. The extent of this effect can be determined only experimentally.

Constant Pressure vs. Constant Rate.—These equations show that for *homogeneous* sludges constant pressure filtration is better than constant rate. On the other hand the initial velocity in a constant pressure operation is so high that it is very likely to cause the filtrate to run cloudy. Even in constant pressure runs it is therefore better to start at low and substantially constant rate until a thoroughly formed layer of sludge is deposited on the filtering medium.

The maximum allowable pressure which can be tolerated in a filtering operation is determined by the strength of the filtering medium or by the tendency of the sludge to force its way through the filter. The higher the pressure the less the life of the filter cloth and the greater the tendency towards cloudiness. In highly compressible sludges the gain by increased pressure is so slight that it is wise to restrict the pressure to a low figure. This maximum advisable pressure must, however, be determined experimentally with each individual sludge.

Determination of Coefficients.—The equations indicate that for non-homogeneous sludges constant rate or constant pressure gradient filtration is far superior to constant pressure, the advantage being the greater the larger the coefficient of velocity effect. Here also the maximum pressure permissible is determined by the danger of rupture of the filtering medium and of cloudiness in the filtrate.

In determining the coefficients for homogeneous sludges it is best in constant pressure runs to plot V^2 versus θ. An error in locating zero time which might otherwise affect the computations will thus be made apparent. By comparison of the slopes of two or more such curves each at different pressures one can compute s and from this, r'. For constant rate runs whether the sludge is homogeneous or not, plot P against V on logarithmic paper. The slope is $1-s$ and from any one point on the curve of a homogeneous sludge one can compute r'. For a non-homogeneous cake, t must be estimated from a second run at a different rate or from a constant pressure run.

Where the filter-aid or other granular material is sufficiently large in amount relative to the slimy material to form a skeleton the volume of the voids of which is greater than the slime can fill, it is obvious that the sludge as a whole is but slightly compressible (*i.e.*, $s=0$). This is usually the case, since if less filter-aid be added the voids in the cake will not be increased and filtration resistance will not be reduced. Consequently it is usually

allowable to make this simplifying assumption where filter-aids are used. Accordingly the pressure gradient, P/V, should be constant in constant rate runs, and experimental data check this conclusion.

Press Resistance.—It must be noted that these equations contain no term for press resistance. Consequently in constant rate runs the term P of the equations is the gauge pressure less the pressure on the press at the start of the run. In constant pressure runs on sludges of low resistance (low values of r) the press resistance term, ρ/A, should be added to the denominator of Eq. (4) before integration.[1] Usually, however, where the resistance of the sludge is at all high this correction term is small enough so that the equations may be used as they stand, especially where applied to the final conditions of the filtration cycle rather than to early points of a run. Since this is the way they are used in engineering design it is better to leave the equations in their simpler form, but to keep in mind the limitations to their use.

The significance of these equations (see p. 366) and their application to a consideration of the factors which control the choice of a filter press for a given operation may be best understood by a somewhat detailed discussion of the following problem.

Illustration 1.—A precipitate of ferric and aluminum hydroxides is being filtered at substantially constant pressure in a chamber press having distance frames 3 ft. square and 1 in. thick. At the pressure used 4.5 cu. ft. of filtrate per sq. ft. of filtering area are obtained before the frames are full. The cake is not washed, 6.5 hours are required to fill the press, and 40 minutes to dump, clean and reassemble it.

(*a*) It is desired to wash the cake in this press with an amount of wash water equal to one-third that of the filtrate. If this be done, how much will the present filtering capacity of the press be reduced?

A new press is to be purchased, which may be of the chamber or leaf type. The chamber press will be 3 ft. square as before. The leaf press will require

[1] Correcting for press resistance, the integrated formulas for constant pressure are:

Homogeneous Sludges:

$$r'vP_i^s(V/A)^2=2P_i\theta-2\rho(V/A).$$

With Filter-aids or Equivalent:

$$\left[\frac{r''vVP_i^t(1+t)}{A}+\rho^{1+t}\right]^{\frac{2+t}{1+t}}=r''v(2+t)P_i^{1+t}\theta+\rho^{2+t}.$$

twenty minutes for dumping and reassembling, and fifteen minutes for filling with wash water and removing excess. It is understood that the new press is to be operated at the present capacity and pressure (practically constant).

Parts *b* and *c* postulate a chamber press; parts *d* and *e* assume that a leaf press will be employed.

(*b*) For maximum filtration capacity without washing what thickness distance frames should be specified for the chamber press?

(*c*) If the cake is to be washed with an amount of water equal to one-third of the filtrate, what thickness distance frames should be provided for maximum capacity?

(*d*) Using a leaf press, how many square feet of filtering area are needed to equal the filtration capacity of 1 sq. ft. of the present press, at the same time giving maximum filtering capacity without washing?

(*e*) The same question but assume the cake to be washed with an amount of water equal to one-third the filtrate.

Assume that the cost of the two types of press including installation expense, is \$2.50 per sq. ft. of filtering area for the chamber press, and \$6.50 for the leaf press. Assume the total charge against investment, including interest, depreciation, maintenance, etc., is 45 per cent per year. The operating costs including overhead are 0.014 cent per hour per sq. ft. of filtering area while filtering and washing and 0.11 cent per hour per sq. ft. while dumping and reassembling.

(*f*) If the presses are in operation 280 days per year, 10 hours per day, what thickness of frames is to be specified for the chamber press, and what thickness of cake should be formed on the leaf filter?

(*g*) The same questions if the presses are operated 24 hrs. per day for 360 days in the year?

Solution.—The relationship between the volume of filtrate discharged, V, in the time θ, through the filtering area of the press, A, working at the pressure P, is expressed by $V^2=2kA^2P\theta$. Since in this problem the pressure remains constant, P may be disregarded and the equation simplified to

$$\frac{V^2}{A^2}=K\theta.$$

Choosing as the basis of calculation the area of the present press, $\theta=6.5$ hours and $V/A=4.5$. Solving, K is found to be 3.12.

The calculation is simplified by calling the thickness of the cake one nth of one inch; *i.e.*, if the cake be one-third of an inch thick, n equals 3. The capacity measured in filtrate then becomes "$4.5/n$" cu. ft. for each sq. ft. of filter cloth, and the frame must be filled n times to obtain the required 4.5 cu. ft. of filtrate; that is, the press must be operated through n cycles to perform the present duty.

In considering the question of maximum capacity and minimum cost it is advisable to tabulate the controlling factors as a function of some definite variable. In this case one will find how the time and cost for this definite amount of filtrate vary with the thickness of filter cake, and in so doing determine the following data:

TABLE I

TIME SCHEDULE, CHAMBER PRESS (Basis = 1 sq. ft.).

No. of cycles	Thickness of distance frame, $1/n$ inches	Filtering time per cycle	Washing time per cycle	Dumping time per cycle	Total time for n cycles (no washing)	Total time for n cycles (with washing)
		Time in hours				
1	1	6.5	17.33	0.67	7.17	24
2	$\frac{1}{2}$	1.62	4.33	0.67	4.59	13.2
3	$\frac{1}{3}$	0.72	1.92	0.67	4.17	9.93
4	$\frac{1}{4}$	0.41	1.08	0.67	4.32	8.64
5	$\frac{1}{5}$	0.26	0.69	0.67	4.65	7.95
6	$\frac{1}{6}$	0.18	0.48	0.67	5.10	8.0
8	$\frac{1}{8}$	0.10	0.27	0.67	6.16	8.3

Differentiating the above equation, the rate of filtration at a given time is $dV/d\theta = 3.12A^2/2V$. Inserting the value of V at the *end* of a filtering cycle for any frame thickness "$1/n$," one obtains the rate of filtration which existed at this time. Obviously the rate will also be the washing rate for a leaf press with a filter cake of thickness $1/n$; but for a chamber press the washing rate will be but one-fourth of this value, because washing is carried on through a cake twice as thick as that through which filtration has proceeded, and the effective filtering area is but one-half as great.[1]

The method of calculating the above data may be understood by taking as an example one thickness of frame; for example, n equals 4. Using the equation

$$\frac{V^2}{A^2} = 3.12\theta,$$

with the ratio $\frac{V}{A} = \frac{4.5}{4} = 1.125$ (since the cake thickness is but one-fourth that employed when 4.5 cu. ft. were obtained), the time is 0.41 hrs. The rate of filtration at the end of the filtering period is obtained from the equation [2]

$$\frac{dV}{d\theta} = \frac{3.12A^2}{2V},$$

[1] This neglects any difference in viscosity between solution and wash water.

[2] It may help in visualizing this equation to write it

$$\frac{d(V/A)}{d\theta} = \frac{3.12}{2(V/A)}.$$

as 1.39 cu. ft. per hr. per sq. ft. of filtering area. The rate of washing in the chamber press is one-fourth this quantity, or 0.347. The volume of the wash water is, $\frac{1.125}{3}$ or 0.375 cu. ft. per sq. ft., and the time of washing is this latter figure divided by the preceding one, or 1.08 hrs. The time required per cycle for filtering, washing and dumping is therefore 2.16 hrs., and the total time to do the work of a one-inch frame, *i.e.*, to produce 4.5 cu. ft. of filtrate per sq. ft. of filtering area, is 8.64 hrs.

Since cost data are given on a basis of one square foot of filtering area, this basis is adhered to in figuring costs. For a chamber press operated 2800 hours per annum the investment charges are $\frac{250\ (0.45)}{2800} = 0.0402$ cent per hr. per sq. ft. of filtering area and similarly for a leaf press 0.1045 cent. Therefore in a chamber press the total cost per hour per sq. ft. of filtering area for filtering and washing is $0.0402 + 0.014 = 0.0542$ cent and for dumping $0.0402 + 0.11 = 0.1502$ cent. The corresponding figures for a leaf press are 0.1185 and 0.2145 cent.

Costs are obtained by multiplying the time required for each operation by the cost of that operation, and the following data results:

TABLE II

COST SCHEDULE, CHAMBER PRESS (Basis = 1 sq. ft.), n cycles

(280 Days, 10 Hours per Day)

No. of cycles	Thickness of distance frame, $1/n$ inches	Filtering cost per n cycles, cents	Washing cost per n cycles, cents	Dumping cost per n cycles, cents	Total cost no washing (n cycles), cents	Total cost with washing (n cycles), cents
1	1	0.352	0.94	0.1	0.452	1.392
2	$\frac{1}{2}$	0.176	0.469	0.2	0.376	0.845
3	$\frac{1}{3}$	0.117	0.312	0.3	0.417	0.731
4	$\frac{1}{4}$	0.0882	0.235	0.4	0.488	0.725
5	$\frac{1}{5}$	0.0705	0.187	0.5	0.571	0.759
6	$\frac{1}{6}$	0.0587	0.156	0.6	0.659	0.815
8	$\frac{1}{8}$	0.0433	0.117	0.8	0.843	0.960

It will be noted that whereas without washing, *maximum capacity* was obtained with a one-third inch frame, *minimum cost* is obtained with a one-half inch frame; while with washing maximum capacity is secured with a one-fifth inch frame, and minimum cost with a one-quarter inch frame.

The methods of calculation for a leaf filter are entirely similar. The filtering time for such a filter will be the same for a half-inch thickness of cake

as for a one-inch distance frame in a chamber filter, since with 1 in. frames the final filtrate flows through a thickness of ½ in. The results are given in the following tables, together with the costs for both chamber and leaf presses when operated 24 hrs. per day, 360 days per year.

TABLE III

TIME SCHEDULE, LEAF PRESS (Basis = 1 sq. ft.)

No. of cycles	Thickness of cake, inches	Filtering time per cycle	Washing time per cycle	Dumping time per cycle	Change time per cycle	Total time for n cycle (no washing)	Total time for n cycle (with washing)
		Time in hours					
1	½	6.5	4.33	0.33	0.25	6.86	11.44
2	¼	1.62	1.08	0.33	0.25	3.90	6.56
3	⅙	0.72	0.48	0.33	0.25	3.17	5.36
4	⅛	0.41	0.27	0.33	0.25	2.96	5.04
5	1/10	0.26	0.17	0.33	0.25	2.95	5.05
6	1/12	0.18	0.12	0.33	0.25	3.06	5.28
8	1/16	0.10	0.066	0.33	0.25	3.44	5.96

TABLE IV

COST SCHEDULE, LEAF PRESS (Basis = 1 sq. ft.)

(280 Days, 10 Hours per Day)

No. of cycles	Thickness of cake, inches	Filtering cost per n cycle, cents	Washing cost per n cycle, cents	Dumping cost per n cycle, cents	Change cost per n cycle, cents	Total cost, no washing (n cycle), cents	Total cost, with washing (n cycle), cents
1	½	0.770	0.513	0.071	0.054	0.841	1.408
2	¼	0.385	0.257	0.143	0.107	0.528	0.892
3	⅙	0.257	0.171	0.215	0.161	0.472	0.804
4	⅛	0.193	0.128	0.286	0.215	0.479	0.822
5	1/10	0.154	0.103	0.357	0.268	0.511	0.882
6	1/12	0.128	0.085	0.427	0.322	0.555	0.962
8	1/16	0.095	0.063	0.569	0.429	0.664	1.156

TABLE V

COSTS OF CHAMBER PRESS (Basis = 1 sq. ft.)

(360 Days, 24 Hours per Day)

No. of cycles	Thickness of distance frame, $1/n$, inches	Filtering cost per n cycles, cents	Washing cost per n cycles, cents	Dumping cost per n cycles, cents	Total cost, no washing (n cycles), cents	Total cost, with washing (n cycles), cents
1	1	0.176	0.468	0.082	0.258	0.726
2	½	0.0875	0.234	0.164	0.252	0.486
3	⅓	0.0583	0.156	0.246	0.304	0.460
4	¼	0.0443	0.117	0.328	0.372	0.489
5	⅕	0.0351	0.093	0.41	0.445	0.538
6	⅙	0.0292	0.078	0.492	0.521	0.599
8	⅛	0.0216	0.058	0.656	0.688	0.746

TABLE VI

COSTS OF LEAF PRESS (Basis = 1 sq. ft.)

(360 Days, 24 Hours per Day)

No. of cycles	Thickness of cake, inches	Filtering cost per n cycles, cents	Washing cost per n cycles, cents	Dumping cost per n cycles, cents	Change cost per n cycles, cents	Total cost, no washing (n cycles), cents	Total cost, with washing (n cycles), cents
1	½	0.311	0.207	0.048	0.036	0.359	0.602
2	¼	0.155	0.104	0.096	0.072	0.251	0.427
3	⅙	0.104	0.069	0.144	0.108	0.248	0.425
4	⅛	0.078	0.052	0.192	0.144	0.270	0.460
5	1/10	0.062	0.042	0.239	0.180	0.301	0.523
6	1/12	0.052	0.034	0.288	0.216	0.340	0.590
8	1/16	0.038	0.025	0.384	0.288	0.422	0.735

It will be noted that *maximum capacity* is secured in this leaf filter without washing with a 1/10-in. thickness of cake corresponding to a ⅕-in. distance frame in the chamber press. With washing the maximum comes at substantially the same point. Both with and without washing the *minimum cost* for 10 hrs. per day comes at one-sixth inch thickness of cake corresponding to a one-third inch distance frame. The fact that in both presses it pays to build up a

thicker cake than corresponds to maximum capacity is due to the saving in labor charges secured at the expense of lowered press capacity.

Notwithstanding the fact of nearly three-fold apparatus cost on the leaf filter the actual filtering cost is only slightly higher than that of the frame press on a 10-hr. basis, and lower on a 24-hr. basis.

The method of charging up such items as depreciation, maintenance, rental of floor space, etc., as a flat percentage against investment cost is open to criticism. The same statement applies to expressing the dumping cost of a leaf press as proportional to its size. The fact is that the character of each one of these items will vary from plant to plant and their distribution in calculating costs must be modified accordingly. No method could be given here which will cover the majority of cases but this particular method satisfactorily illustrates the principle.

The answers to the questions as stated, are therefore, as follows:

(*a*) Since the total time for the present press without washing is 7.17 hrs. and with washing 24 hrs., the capacity per hour per sq. ft. will be reduced from $4.5/7.17 = 0.628$ cu. ft. per hr. to $4.5/24 = 0.1875$ cu. ft. per hr., a reduction of 70 per cent.

(*b*) From Table I it will be noted that the total time without washing is a minimum for one-third inch distance frames.

(*c*) The time with washing is seen from Table I to be a minimum when using $\frac{1}{5}$ in. distance frames.

(*d*) With a leaf filter the filtering time without washing is a minimum with $\frac{1}{10}$ in. thickness of cake, filtration being completed in 2.95 hrs. Since the present press requires 7.17 hrs. it has only 41.1 per cent of the capacity of the new press. Hence the new press will require only 0.411 sq. ft. filtering area for each sq. ft. of the present press.

(*e*) Since the present press requires 24 hrs. for washing while a leaf press will do the work in 5.04 hrs., the present press has only 21 per cent capacity of the leaf press so that the size of leaf press required will be only 0.21 sq. ft. of filtering area per sq. ft. of area in the present press.

(*f*) Inspection of Table II shows that the minimum cost of filtration in a chamber press without washing is obtained with $\frac{1}{2}$-in. frames and with washing by the use of $\frac{1}{4}$-in. frames.

The minimum cost with a leaf press *without washing* is found in $\frac{1}{6}$-in. thickness of cake. This gives a total filtration time of 3.17 hrs. as compared with 7.17 hrs. in the present press, *i.e.*, the present press has 44.3 per cent the capacity of the proposed leaf filter. This means that the new filter must have 0.443 sq. ft. of filtering area for each sq. ft. in the present press. *With washing*, the capacity of this new press is therefore such that 0.223 sq. ft. of filtering area will suffice in place of 1 sq. ft. in the present press.

The preceding paragraph must not be interpreted to mean that the capacity of a leaf filter so greatly exceeds that of a frame press. The comparison should be made, not with the present press, the frames of which are too thick, but with the chamber press at its best, *i.e.*, when using $\frac{1}{2}$-in. frames without washing and $\frac{1}{4}$-in. frames with washing, requiring 4.59 hrs. and 8.64 hrs. respectively, as compared with the 3.17 hrs. and 5.36 hrs. required for the leaf press. In other words, the capacity of the chamber press is 69.1 per cent of that of the leaf press without washing and 62 per cent with washing. This means that the investment cost of a leaf press is correspondingly reduced.

(*g*) Inspection of the tabulated costs for full time work shows the thicknesses should remain unchanged except for washing in the chamber press, which should now be done with $\frac{1}{4}$-in. frames. While all costs are lowered, the leaf press now has the advantage over the chamber press. It may be stated in general that large scale and continuity of operation tend to give the advantage to the leaf type of press.

It must not be forgotten that the numerical comparisons of the preceding paragraphs are dependent on the operating conditions and costs assumed and any variation in these will influence the results. However, the character and direction of the influence of these factors on the relative advantages of the two types will remain in all cases the same.

The utilization of the equations for non-homogeneous sludges may be illustrated by the following problem:

Illustration 2.—A slimy precipitate is filtered by admixture of a definite proportion of infusorial earth. Filtrations are carried out at substantially constant rate. The average filtration rate of each press is 158 cu. ft. of filtrate per hr. The average length of filtration for each press is 1.96 hrs., the total filtrate therefore being 310 cu. ft. The pressure reached at the end of the filtration period averages 14.5 lbs. per sq. in. The rate is then increased for several days to an average of 194 cu. ft. per hr. when it is found that approximately the same volume of filtrate, more exactly 303 cu. ft. per press, is obtained in 1.56 hrs., when the pressure has built up to 46 lbs. It requires 18 min. to dump and refill this press. At what rate should this press be operated in order to get the maximum average capacity, assuming that a maximum pressure of 50 lbs. is allowable?

Since the press has a definite area, which it is not proposed to change, and is handling a liquor with a definite concentration of sludge, the filtration equation for this case, Eq. (4*b*), reduces to,

$$(V/\theta)^{1+t} = KP/V.$$

Since it is desired to have the average capacity as large as possible, one must have $V/(\theta+a)$ a maximum, where a is the time lost in dumping and filling. Eliminating θ by means of the former equation, differentiating this expression and placing the differential coefficient equal to zero, one finds that the equation for maximum filtration velocity is

$$(V/\theta)^{2+t} = KP/a(1+t).$$

Applying the first equation to the two sets of data in succession, dividing one equation thus obtained by the other and solving for t, one finds $t = 4.7$. From either of these expressions the value of K is found to be $7.3\ (10)^{13}$. Inserting these quantities into the equation for optimum filtration velocity one obtains 194 cu. ft. per hr. In other words, the second of the two rates employed happened to be the maximum rate.

CHAPTER XII

BASIC PRINCIPLES OF VAPORIZATION PROCESSES

INTRODUCTION TO EVAPORATION, DISTILLATION, AND DRYING

That property of liquids by virtue of which they pass from the liquid to the vapor state, or the reverse, according to the temperature and pressure to which they are subjected, is the basis of very important industrial processes for separating one liquid from other liquids, or liquids from solids.

Industrial terminology distinguishes three cases in which separation is accomplished by utilizing differences in the volatility of substances, and while the classification is not a rigorous one and is sometimes illogical, it will be adopted for the purpose of a general sub-division of this field into three chapters.

Evaporation is the removal by vaporization of a portion of the solvent from a solution of a solid or a practically non-volatile liquid, when the vapor formed is valueless in comparison to the residue (except perhaps for its heat content). Since water is the only liquid which can be obtained in unlimited quantity, and hence can be economically discarded, evaporation processes are limited in practice to water solutions; for example, the concentration of aqueous solutions of inorganic compounds, glue, tannin, sugar, sulfuric acid, etc.

Distillation [1] is the removal by vaporization of one liquid from another when the vapor is of sufficient value to warrant recovery by recondensation. For example, the removal by vaporization of water from its impurities, of stearic acid from unsaponifiable matter, of alcohol from water, gasolene from kerosene, benzene from toluene, of benzene from mineral oil, of gasolene from extracted wool grease, etc., are distillation processes.

[1] Under the term *destructive distillation* are described those processes in which the material acted upon, such as wood, coal or bones, is first decomposed by heat, and the volatile products of the reaction then drawn off and recovered.

When one solid is separated from other solids by vaporization and subsequent condensation the process is spoken of as sublimation. Phthalic acid, for example, is purified by sublimation.

Drying is the removal, generally by vaporization, of one liquid from another liquid or from a solid, when the amount of the liquid to be separated relative to that which remains, or to the solid, is small, and generally worthless. For example, drying is represented by the vaporization of water from sand, ores, coal, leather, paper, vulcanized fibre, fibre board, leather board, textiles, twine, starch, sugar, wet crystals; again by the vaporization of carbon bisulphide from thio-carbanalide crystals, benzene from dipped rubber goods, organic solvents from impregnated and lacquered substances, emulsified water from oil, and the like. In the chapter on Drying, certain cases have been included where the separation is accomplished without resorting to the process of vaporization. While such cases should logically be classified under Mechanical Separation, the name Drying has been so firmly associated with these operations that they are taken up under this heading.

Certain inconsistencies exist in practical terminology which the reader must not take too seriously. For example, when water is separated from sea-water in order to obtain the dissolved salt, the process is called evaporation; when it is the recondensed vapor which is wanted, *i.e.*, pure water, the process is called distillation. The apparatus employed in the two cases may, however, be practically identical. When the amount of water associated with alcohol is large, it is separated by distillation; when small, it is separated by drying with anhydrous copper sulphate. The vaporization of water from a glycerine solution is called evaporation although the apparatus used where glycerine loss must be avoided is identical with that employed for distillation.

These three processes have certain elementary principles in common. In order to lay a foundation for the development of the engineering problems involved in their consideration, these principles will be considered somewhat in detail.

MECHANISM OF VAPORIZATION

Vapor Pressure.—The molecules of a liquid are considered to be in a state of constant unordered motion, some moving

with great velocity, while others move relatively slowly. For any temperature, however, there is a certain mean velocity of the molecules, which for temperatures below the boiling point of the liquid, is not sufficient to project them beyond the free surface of the liquid. But there are always some molecules which possess a velocity sufficiently greater than this mean, that, when they approach the free surface of the liquid, they overcome the mutual attraction exerted between them and other molecules in the liquid, and continuing their motion, pass out into the surrounding space, and exert a pressure upon the walls of the container as the resultant of the bombardment which their motion produces. Since they move in all directions, a certain number will strike the liquid surface from which they emanated, and again become a part of it. When the number of molecules re-entering the surface is just equal to that leaving it, a condition of dynamic equilibrium exists. This portion of the substance is then said to be in vapor form, or phase, and the pressure exerted upon the walls of the container by these molecules is called the *vapor pressure*[1] of the substance at the existing temperature.

If the space surrounding the liquid be filled with molecules of some other substances, *e.g.*, air, at a pressure not materially exceeding one atmosphere, the voids between particles are sufficiently large and numerous to enable the above described phenomenon to take place undisturbed. Since the pressure on the container is due to the sum of the molecular impacts, there will be present a final pressure made up of the pressure of the gas originally present plus the vapor pressure of the liquid. Should the liquid possess that attraction for the molecules of the original gas which results in solution, this relationship no longer holds; nor is it valid if the original gas is under a high pressure.[2]

If a liquid be made up of two kinds of substances *mechanically mixed* but of low mutual solubility, for example, benzene and water, each will give off its individual molecules, and each will establish an equilibrium between the escaping and returning molecules of its own kind, and hence a vapor pressure of its own independent

[1] This is also called the "pressure of the saturated vapor" or "saturation pressure."

[2] Deviations from the gas laws usually become large when the pressure is a considerable fraction of the saturation pressure of the liquefied gas. (See p. 7.)

of the presence of the other molecules. These pressures are additive and the sum of these partial pressures plus that of any gas originally present makes up the total pressure within the container.[1] In other words, the mixture behaves as though the surface were alternately entirely one liquid and then the other.

Vapor Pressure Lowering.—When the substances or components making up a liquid are mutually soluble, as for example alcohol and water, the escaping tendency of each substance is reduced due to the presence of the other. The partial pressure of each, and since they are additive the total vapor pressure of the liquid, is thereby reduced. Even when one of the substances, for example, salt, has itself a negligible vapor pressure, it nevertheless when dissolved in water reduces the vapor pressure of the latter. On the other hand if the molecules of the dissolved substance be very large the reduction in vapor pressure of the solvent is negligible.

It is important to visualize the reason for these facts. Assume an equimolal solution of naphthalene dissolved in benzene. At ordinary temperature the volatility of the naphthalene relative to that of benzene may be neglected. Furthermore there is good reason to believe that the size of the naphthalene molecule is not far from that of the benzene molecule. In the surface of such a solution approximately one-half of the area is therefore occupied by benzene and one-half by naphthalene molecules. The chance for benzene molecules to escape from the solution into the vapor space is therefore only half what it is in pure liquid benzene. In order to have equilibrium with benzene vapor it is therefore necessary for the vapor pressure above this solution to be only half that of pure benzene. The reason for this is that any benzene molecule coming from the vapor toward the surface of the liquid at high velocity will force its way into the liquid whether it hit a benzene molecule or naphthalene molecule in the surface of the liquid, because the difficulty of forcing either of these two out of the way is approximately equal.

On the other hand assume a solution of glue and water of such concentration that one-half the surface of the liquid is occupied by glue molecules. If now a water molecule from the vapor space impinge upon the surface of the liquid it will force its way into the liquid if it happens to hit a water molecule in the liquid surface. If, however, it hits a glue molecule, this is so heavy that it cannot displace it and it is simply reflected back into the vapor. The situation is much the same as though one-half the surface of the liquid water were

[1] If the mixture be not agitated two layers will form and the lower liquid will vaporize through the upper much more slowly than if freely exposed. On the other hand the evaporation is more rapid than might at first appear because the lower liquid dissolves to a finite extent in the upper and is carried by convection currents to the exposed surface where it evaporates.

covered with a sheet of glass. The result is that only half the liquid surface is available for entrance of water molecules from the vapor space. Consequently the full vapor pressure of water is necessary in the vapor space in order to maintain equilibrium.

An interesting corollary of the phenomenon is that whereas water solutions of glue exert substantially the full vapor pressure of pure water, the rate of evaporation of water from the surface of such a solution is but a fraction of that from the surface of pure water. On the other hand the rate of evaporation from solutions in benzene of materials of moderate molecular weights is proportional to the partial pressure of benzene in the solution. In paint and varnish removers this principle is utilized by adding to the volatile solvent which one wishes to have remain on the exposed painted surface, a small amount of some substance of high molecular weight which will concentrate on the surface of the solvent and greatly reduce its rate of evaporation.

It will be noted that the molecular weight of the glue is so high that the mol fraction of glue is negligible. One can generalize the preceding facts by saying that the partial pressure of a volatile material in a solution is proportional to its mol fraction, but the rate of vaporization will be proportional to its partial pressure if the molecular weights of other materials in the mixture are low. On the other hand the rate of vaporization of the components in question will be less than corresponds to their partial pressures if the other components are of extremely high molecular weights.

Heat of Vaporization.—If the molecules escaping from the surface of a body pass into air or other inert gas within a container, there is first formed this condition of equilibrium upon the inner surface of the relatively stationary gas film with which every surface is surrounded. (See Chapter II, Fluid Films.) From the outer surface of this film the molecules pass into and throughout the remaining space by both their own motion (diffusion) and by convection, until equilibrium is established in the entire container. Through the film itself they pass by diffusion. When the container is not closed, both diffusion and convection processes carry the vapor from the surface of the stationary film into the outside air, which is to a corresponding extent pushed back into space, and the normal atmospheric pressure is maintained. This total atmospheric pressure is now made up of the vapor pressure of the substance (which when equilibrium is reached is the same as though no air were present), and that amount of air which has not been driven back.

Therefore, in order for vaporization to continue at a constant temperature, the dynamic equilibrium which tends to establish itself must be destroyed. If the surface of the substance be exposed to the atmosphere, the molecules arising from it may be

swept away by a current of air; this takes place in air drying, and during evaporation of liquids into air. If the containing vessel be closed, these molecules will pass to a region of lower pressure, *i.e.*, where there are fewer of them. Such a region may be maintained by constantly removing the vapor molecules by dropping the temperature, thus decreasing the number and also the velocity of the molecules, and hence the resultant pressure, as in a condenser; or by being pumped out mechanically as in the "vapor compression" system of evaporation (p. 407), or by absorbing the molecules in a medium which has for them a great attraction, *i.e.*, a medium which they will enter by impact, but from which they cannot return; such as drying over sulphuric acid and the like.

A constant temperature is not maintained of itself within a volatilizing liquid. Those molecules having the greater velocity, possess also the greater amount of kinetic energy. Hence as these leave the liquid its mean kinetic energy decreases, and the temperature falls. In order to maintain a definite temperature, therefore, heat must be added from an external source. This heat of vaporization varies with the substance, somewhat also with the ratio of pressure to temperature. The molal heat of vaporization (the specific heat of vaporization multiplied by the molecular weight) for all liquids at their boiling point is of the same order of magnitude. The exact relation between heat of vaporization, molecular weight, temperature and pressure is given by the Hildebrand function. (See Fig. 6, p. 16.)

Boiling Point.—Since molecular motion is a function of temperature[1] obviously the more energy with which a molecule is endowed, that is the hotter it is, the more rapidly will it move, and hence the greater will be its vapor pressure. There must then be a temperature where the escaping molecules of a substance will maintain a pressure of their own equal to the atmospheric pressure. The air can then be forced back indefinitely and the substance vaporize indefinitely so far as pressure is concerned. This temperature is called the *boiling point* of the substance.

[1] According to Smithsonian Tables (p. 399, 1920 Ed.) the mean velocity of gas molecules in feet per second equals $386\sqrt{T/M}$, where T is the °F. absolute temperature and M is the molecular weight. Thus the mean diffusional velocity of air at 70° F. and normal barometer would be 1650 ft. per second, or 1130 miles per hour.

FACTORS CONTROLLING VAPORIZATION

If the liquid is in a space in which the partial pressure of its vapor is less than the vapor pressure it possesses at this temperature, it will proceed to vaporize and its vapor will pass into space. But this change of state is accompanied by the large absorption of heat already noted. If this heat be not supplied from some external source, vaporization will nevertheless continue, and the necessary heat will be taken from the sensible heat of the liquid, with a consequent reduction of temperature. This fall in temperature of the liquid is accompanied by a corresponding decrease in vapor pressure. Finally a temperature is reached where the vapor pressure of the liquid is equal to its partial pressure existing in the space and vaporization will cease.

Therefore, in order for vaporization to continue, two conditions must be met:

First—the heat necessary for vaporization must be continuously supplied.

Second—the equilibrium which forms between the vapor pressure of the liquid and its partial pressure in the surrounding space must be continuously destroyed.

If either one of these two conditions be neglected vaporization will be retarded or even stopped.

CAPACITY

In all three processes (evaporation, distillation, and drying) the rate of vaporization, and hence the capacity, is determined by the rate of heat supply. Where the heat is transferred by conduction and convection, as is often the case, the capacity is determined by the following integrated form of Newton's law:

$$\frac{Q}{\theta} = (H)\ (A)_{av}\ (\Delta t)_{av},$$

where $\frac{Q}{\theta}$ = B.t.u. transferred per hour.

An inspection of this equation shows that the capacity (Q/θ) is determined by the product of three factors:

A_{av} = A proper average area of heating surface in sq. ft.

$(\Delta t)_{av}$ = A proper average overall temperature difference in °F. between the points from and to which heat is flowing, and

H = Overall coefficient of heat transfer, which may be experimentally determined, or estimated from a knowledge of each of the resistances to be encountered. (See p. 134 to 157.)

Where heat is transferred by radiation, the rate of heat supply is determined by

(*a*) the area of the surface exposed to the radiant heat,

(*b*) the difference of the fourth powers of the absolute temperatures,

(*c*) the black body coefficients of the surfaces.

Where heat is being supplied by both mechanisms, the rate of flow of heat is calculated by adding the rates figured by the appropriate equation for each process.

For general discussion of the equations, data and illustrative examples for these mechanisms, the reader is referred to the chapter on Flow of Heat. However, the mechanism by which heat is carried into a vaporizing liquid, and by which the vapor forming on the surface of the liquid is removed, is so controlling in all these processes, that it will be considered in detail in the three following chapters.

CHAPTER XIII

EVAPORATION

BASIC FACTORS

To secure the evaporation of a volatile liquid, there are two and only two essentials that must be provided:

First, the necessary heat of vaporization must be supplied to the liquid:

Second, the vapor evolved must be removed from above the surface of the liquid and not allowed to accumulate.

1. Heat Supply.—It is necessary to supply the heat into the liquid itself, because the vapor bubbles are developed there, and at the instant of their formation absorb the heat incident to their evolution. The heat may be supplied in two ways:

(*a*) By direct exposure of the liquid to the source of the heat.

(*b*) Indirectly by transmission through a suitable solid retaining wall.

2. Vapor Removal.—The vapor evolved may be carried away in two conditions:

(*a*) Mixed with an inert gas (*e.g.*, air, flue gas, etc.).

(*b*) As undiluted vapor.

CLASSIFICATION OF EVAPORATION PROCESSES

Since there are two ways of supplying the heat and two conditions in which vapor may be removed, there are four combinations possible:

Case I: The heat is supplied through the free surface of the liquid, and the vapor is carried away by an inert gas.

Case II: The heat is supplied through the free surface of the liquid, and the vapor is evolved in undiluted form.

Case III: The heat is transferred through solid retaining walls to the liquid, and the vapor is swept away by an inert gas.

Case IV: The heat is transferred through solid retaining walls to the liquid, and the vapor is evolved in undiluted form.

The various evaporation processes will be classified under these four subdivisions.

CASE I

The Heat is Supplied Directly through the Free Surface of the Liquid, and the Vapor is Swept away by an Inert Gas.

Evaporators in which the heat is supplied through the disengaging surface of the evaporating liquid, possess the advantage that the apparatus may be built of material chosen with special regard to its resistance to corrosion irrespective of its heat conductivity, that the evaporator is practically unaffected by incrustation of solids depositing from the liquid, and that, when the initial source of heat is a hot, inert gas, the heat transfer may be direct from the source to the liquid. The main limitation of this type is that hitherto no one has succeeded in adapting it to utilize the multiple-effect principle.

1. Solar Evaporation.—The cheapest, although in most localities least reliable, source of heat is the sun. Here the heat is transferred directly into the liquid by *radiation* from the sun, and also to the liquid surface from the air by convection. Salt solutions are sometimes concentrated in shallow rectangular pans by this method.

2. Ricks.—A simple evaporator of this type consists of piles or "ricks" of brushwood over which salt solution trickles from distributing troughs above, and the concentrated brine is collected in drains below, the evaporation being accomplished largely by the wind. Covers are unnecessary in this case, as during rain the flow of brine is discontinued. The gypsum in the brine soon covers the twigs with thick incrustations, and the ricks eliminate a large amount of this troublesome material.

3. Porion Evaporator.—An efficient apparatus using an artificial heat supply is the Porion evaporator. This consists of a horizontal chamber on the bottom of which flows the liquid to be evaporated, while above it the flue gases from the furnace underneath pass in an opposite direction. The liquid is given a

large surface and intimate contact with the hot gases, being thrown by centrifugal force in the form of drops into the gaseous space by a series of disks, on a rapidly rotating shaft placed crosswise in the evaporating chamber, the disks dipping partly into the liquid below. Because of the high temperature difference realized, and the large surface exposed, the capacity is great; disadvantages are contamination of the liquor with soot and dust from the flue gases.

4. Spray Evaporators.—Evaporation of a solution may be carried to completion and a dry dust obtained by spraying the solution into a chamber against hot gases. This method is said to be quite successful for tannic acid, and the like. If, during their fall, the droplets can be exposed to direct radiation from the fuel bed, evaporation is accelerated and a large capacity realized. Thus, common salt may be so recovered, and the concentrated[1] waste liquor from pulp mills, operating the soda or the sulphate process, may be in this way, not only evaporated, but dried and incinerated. If the spray produces relatively small droplets the resultant dust may be so fine as to present difficulty in its settling, thus causing loss of material up the stack. However, devices are available for recovering such dust, see pp. 329 to 332.

5. Tower Evaporation.—Instead of sub-dividing the liquid into small drops, a large surface may be obtained by passing the liquid in a thin film over bricks or other filling in a tower up which hot flue gas is passing. When oil or dust-free producer gas is used as a fuel no dust is introduced and rapid evaporation is effected.

The Glover tower of a sulphuric acid chamber plant, while fulfilling a number of functions, is an evaporator of this type. Dilute acid is fed to the top and is concentrated as it falls, the evaporation being at the expense of the sensible heat of the hot gases entering the bottom. In recent years installations of this type have been developed for the concentration of dilute sulphuric acid, the acid flowing down over the filling material of a tower, countercurrent to hot furnace gases from an oil burner located beside the bottom of the tower which serves as its flue. (Gilchrist

[1] The dilute waste liquor is concentrated in a multiple-effect system of evaporators to a point such that, when fed into a rotary furnace, the heat evolved in combustion of the organic material is sufficient to evaporate the residual moisture.

Concentration System.) Such an installation is peculiarly suited for this particular operation, because at the high temperature and acid concentration prevailing at the bottom of the tower, relatively large quantities of sulphur trioxide are volatilized. The top of the large tower serves as a combination of rectifying column, partial condenser, and final condenser, wherein this volatilized SO_3 is condensed and reabsorbed, thus avoiding its loss and the serious nuisance created by its escape. In view of the simplicity of the apparatus and the ease of operation, it is surprising that towers of this sort, fired directly with the flue gases from a furnace, are not more widely used.

6. Evaporation by Bubbling Gas through the Liquid.—Notwithstanding the low partial pressure of most liquids at moderate temperature, substantial evaporation can be effected by passing air or other gases through the solution at as high a temperature as the liquid will tolerate without serious decomposition. The air should be injected in very fine bubbles and in large volume. For example, a solution of lactic acid may be thus concentrated without deterioration, due to even moderate heating. The air is effective, not only for carrying away the vapor which springs into the small bubbles as they pass through the liquid, but also for perfect agitation which maintains the liquid at a uniform (maximum) temperature.

CASE II

The Heat is Supplied through the Free Surface of the Liquid, and the Vapor is Evolved in Undiluted Form.

There are no examples of this case in practice. Conceivably, it could be realized by generating radiant heat electrically within a closed still, but such a system has no apparent advantages, while it has obvious disadvantages. The case of evaporating water from a solution or suspension sprayed into a chamber, containing superheated steam will be treated under "Drying."

CASE III

The Heat is Transferred through Solid Retaining Walls to the Liquid, and the Vapor is Swept away by Inert Gas.

This combination is seldom found, except where the evaporator is direct-fired and the flue gases are allowed to flow over the free surface of the liquid. In this case, heat may be transferred

in two ways: conduction through the walls of the evaporator body, and convection from the flue gases to the surface of the liquid in the evaporator. The passage of the flue gas over the surface of the liquid will have no effect in increasing the capacity unless the rate of evaporation is so slow that the vapor is evolved at a pressure below atmospheric, as in the concentration of sulphuric acid in open pans or dishes. In this case, the vapor pressure of the water is much less than one atmosphere because of the vapor pressure lowering caused by the acid. A modification of this case is found in the salt industry in the form of apparatus known as "salt grainers." These grainers comprise large shallow rectangular chambers, built of wood, concrete, or steel, fitted with large diameter tubes with steam on the inside. Steam is admitted at such a rate that no ebullition takes place, the evaporation going on quietly with no disturbance of the liquor surface. Meanwhile salt crystals form on the surface and gradually sink to the bottom of the grainer.

For the evaporation of very corrosive liquids, pans may be constructed of special materials. Thus for the concentration of sulphuric acid above 60° Bé., pans of platinum and gold were formerly widely used, direct-fired, and provided with draft hoods for removal of the fumes. At one time even glass, in the form of large evaporating dishes, was used for this purpose, but the breakage, due both to shock and to unequal heatings, was excessive. In recent years, dishes of fused silica, of various shapes, arranged in cascade, so the acid under concentration flows continuously through the apparatus, have been introduced. To avoid breakage due to unequal expansion of setting and dish, these are placed on rings of asbestos packing in the top of the flue from a suitable furnace, and are thus directly heated by the flue gases. The flow of acid is counter-current to that of the gases, to provide for the rising boiling point of the acid during evaporation. As before, draft must be provided for removal of fumes. These dishes are fragile, and breakage is severe, especially in the expensive larger sizes. It has been attempted to replace them by dishes cast of high silica iron but practice in this field is not yet standardized.

In the production of C. P. chemicals, and other more expensive products, porcelain evaporating dishes up to 18 in. in diameter and 6 in. deep are used; they are resistant, but of poor conductivity, fragile and expensive.

CASE IV

The Heat is Transferred through Retaining Walls to the Liquid, and the Vapor is Evolved in Undiluted Form.

By far the greater part of evaporative equipment falls in this class. The source of heat may be (1) fire or hot gases, (2) hot oil or other liquid, and (3) steam. The most important of these is steam, and the rest of this chapter will be largely devoted to this case.

1. Direct-Fired Evaporators.—These consist usually of a cast-iron pot or steel pan set over a fire. It is well to have combustion nearly complete before the flue gases strike the metal parts of the evaporator body, as the rate of combustion of the unburned gases is greatly decreased when the temperature of the gases is lowered. When the bottom of the evaporator is exposed to the fire, as in a steam boiler, the greater proportion of the heat is transferred by radiation. However, where close temperature control is desired, it may be necessary to forego the rapid rate of heat transfer by radiation and to depend mainly on heating by the hot gases.

The main resistance to the flow of heat in direct-fired evaporators (or stills) is on the combustion side of the evaporator body, and hence stirring of the contents of the evaporator will not greatly increase the capacity. However, positive circulation in the evaporator may be necessary to overcome the tendency of certain parts to become overheated, for example, when a very viscous material is being heated. The capacity depends mainly, then, upon the area of "still" bottom exposed to heat and the difference in temperature between this and the source of heat.

2. Oil Heated Evaporators.—Where a sufficiently high temperature cannot be obtained by using steam at commercial pressures, and where direct-firing is undesirable, the heating is accomplished by the use of hot oil. This method of heating may be applied to practically any form of apparatus designed for heating by means of steam, but usually it is applied to jacketed kettles.

The oil heating system consists in a direct-fired "absorber," which is often similar to a water-tube boiler, together with a number of automatic safety devices designed to prevent overheating of the oil, or "burning out" of tubes in the absorber.

3. Steam Heated Evaporators.—It very frequently happens that steam can be used as a source of heat more conveniently

than the direct combustion of fuel. The devices thus utilizing steam are many, but certain basic conditions must be met for the most economical practice. As previously indicated (p. 386), capacity is directly proportional to the product of the following three factors: area of heating surface, overall difference in temperature between steam and boiling liquid, and overall coefficient of heat transfer from steam to boiling liquid.

In order that the heating surface may be as effective as possible, one must have provision for conducting the condensed steam (water) promptly out of the heating system, and provision for preventing the accumulation therein of the fixed gases carried by the steam.

The value of the overall coefficient of heat transfer, as shown in the chapter on Flow of Heat, depends on a number of variables, such as:

Thermal conductivity of boiling liquid, which is, in turn, mainly determined by its specific heat, specific gravity, and molecular weight (p. 180).

Viscosity of the boiling liquid, which varies with temperature and concentration for a given liquid, and varies widely from liquid to liquid. The importance of this factor can hardly be overestimated.

Effectiveness of convection currents within the boiling liquid, which is determined by the rate of evaporation per unit area of heating surface, by the physical properties of the solution in question, by the depth of liquor on the heating surface, and the relative arrangement of heating surface and liquor space. The importance of the latter will be brought out in the discussion of the various types of evaporator bodies. Since the magnitude of convection currents in a given case depends on the rate of evaporation per unit area of heating surface, the effect of *temperature difference* is obvious.

In Fig. 92 is shown the relation between the overall [1] coefficient of heat transfer, H, the difference in temperature between condensing steam and boiling liquid, Δt, and the viscosity of the boiling solution, z. Since as a first approximation H may be assumed

[1] The controlling factor is the film coefficient from tube to boiling liquid rather than the overall coefficient (p. 136). But since up to a value of about 400 the two are nearly proportional this simplification is valid within this range. Beyond a value of 400 the plot should be used with caution.

inversely proportional to z, the product of the two is plotted as ordinates.

These data are the results of three independent investigations on evaporator bodies of Type 1. It will be noted that the points for each series of runs fall on a straight line on logarithmic paper and that the slopes of these four lines do not differ greatly. The difference in the ordinates for any single value of Δt is due

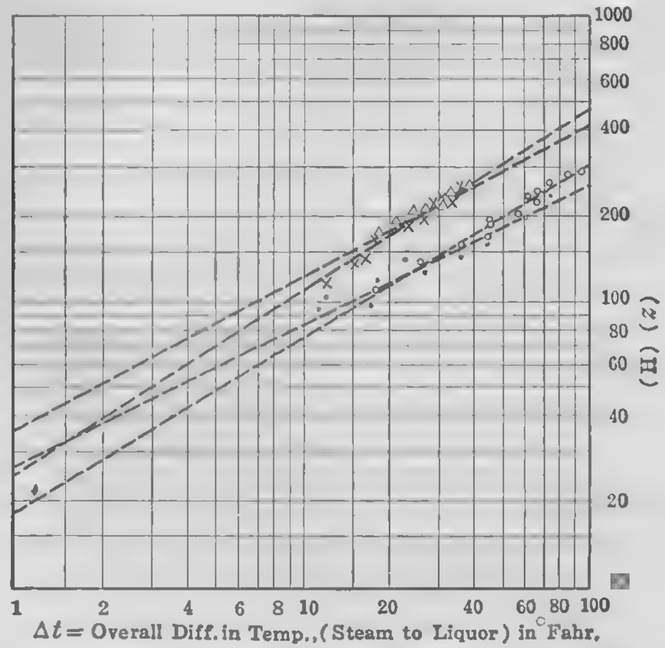


FIG. 92.—(H = Overall Coefficient of Heat Transfer, as B.t.u. per Hr. per Sq. Ft. per °F.; z = Viscosity of Boiling Liquor in Centipoises.)

• *Evaporation of Water, Badger and Shepard, Chem. Met. Eng., 23, 232 (1920).*
○ *Evaporation of Water, Claasen, Zeit. d. Ver. Deut. Ing., 46, 418 (1902).*
△ *Evaporation of Water, Torrey and Pratt, M.I.T. Thesis, 1913.*
× *Concentration of Ten Per Cent Salt Solution, ibid.*

most probably to variations in the degree of circulation occasioned by the disposition of the heating element in the evaporator body, and other variations in construction.

If one has heat transfer and viscosity data for any type of evaporator body operating under definite conditions this diagram may be used to predict the coefficient of heat transfer for the same [1]

[1] Where data for the same liquid are not available one may use as an approximation results obtained with a similar liquid, *i.e.*, one which has the same thermal conductivity (p. 180).

liquid in that evaporator under changed conditions, due to the fact that the curves are practically parallel. This is done by plotting the available data on this diagram and drawing through the point or points a line parallel to the general trend of those shown in Fig. 92. Such a line then represents the values of Hz corresponding to values of Δt for that liquid and type and design of evaporator. Thus if a solution with a viscosity of 0.4 centipoise is boiling in an evaporator with a coefficient H of 375 where the temperature difference is 10° F., a point on the above diagram would fall at absicssa of 10 and ordinate 150. If now this apparatus be operated with this liquid, but at a concentration and temperature where the viscosity is 10 centipoises, and with a difference in temperature of 40° F., the coefficient H may be obtained by seeking on the line just drawn, the ordinate Hz which corresponds with the abscissa of 40. This is found to be about 330, and the coefficient H is approximately 33. While such a value is not absolute, all the available data indicate that it will be far more reliable than that obtained by the present methods of guessing.

Thermal conductivity of the heating surface, through which heat is transferred by conduction.

The thermal conductivity of copper is approximately nine times that of steel, and the thickness of copper tubes is usually about the same as that of seamless steel tubes, so if the thermal resistance of the heating surface were the controlling factor, a nine-fold increase in capacity would be expected upon the substitution of copper for steel tubes. As shown on p. 145, the thermal resistance of metal tubes in an evaporator is small compared to the total resistance, so only a small increase results from such a substitution. Obviously, the less the other resistances in comparison to that of the walls of the heating surface, the greater is the gain, but even under the most favorable conditions, *i.e.*, with practically pure steam condensing on one side, and very rapid circulation of boiling liquor on the other, the gain rarely exceeds 30 per cent and is usually much less. However, where the walls of the heating surface are relatively thick and made of a material of low heat conductivity, such as enameled iron, the overall coefficient from condensing steam to boiling liquid may be considerably less than the value obtained with a thin all-metal wall.

Uniformity of heating, completeness of control and general simplicity of operation are among the advantages incident to steam as a source of heat. Obviously, if low pressure exhaust steam is available, great economy is introduced by its use, even when it is necessary to obtain the desired difference in temperature between the steam and the boiling point of the liquid to be evaporated, by lowering this latter by means of a vacuum.

Jacketed Kettles and Pans.—Apparatus of this type of the most diverse character is now available, and much latitude in size, shape, completeness of agitation of the charge, and material of construction is enjoyed. Many manufacturers supply kettles made of aluminum, duriron, copper, steel and cast iron and also kettles lined with tin, silver and enamel to resist specific corrosive action. Although brittle, enameled ware can be secured of sufficiently high quality to stand up under reasonable service conditions, both as to temperature variation and shock; a drawback is its lower heat conductivity, as noted above.

Standard Evaporator Bodies.—Most of the evaporators in use are those heated by means of steam. Various types are available and these will be discussed in detail in connection with multiple-effect evaporation under the heading "Typical Evaporator Bodies." (See pp. 408 to 416.) However, it should be remembered that such can be and are used for single effect operation, both for continuous feed and discharge, and for operation by the "batch" process.

Evaporation in Vacuum.—There is a very general impression that evaporation can be carried on under a vacuum at a less expenditure of energy than at ordinary atmospheric pressure. The actual saving is little or nothing; for, while less heat is required to bring the liquid to the boiling point, the heat of vaporization increases as the temperature falls (see Hildebrand chart, p. 16 and pp. 432 to 433), and furthermore a certain amount of energy is required to operate the vacuum pump.

The real advantages incident to the use of vacuum, are first, the boiling point of the liquid is reduced, and hence the temperature difference between the boiling liquid and low pressure steam is increased, and evaporation accelerated. Second, many substances, chiefly organic, deteriorate when their solutions are boiled at atmospheric pressure, as, for example, glue and tannin solutions,

milk and concentrated solutions of sugar. Third, the size and character of many crystals may also be controlled by the temperature and rate of formation from an evaporating solution (p. 417).

Maintenance of Vacuum.—As already indicated, operating an evaporator under vacuum increases its capacity because of the increased temperature difference between the source of heat and the boiling liquid. Since the pressure is below atmospheric the vapor must be pumped out, though it is important to condense it before removal, thus reducing the work required to a very small value. Assuming free[1] vapor passages and the absence of non-condensable gases, the total pressure in such a system will be the vapor pressure of the liquid at the lowest temperature to which it is cooled in the condenser, while yet in contact with its vapor. Were the pressure lower, no condensation whatever could take place; were it higher the temperature of the condensed liquid would instantly rise due to condensation of more vapor into it. In general, the pressure in such a system will be somewhat greater than the above owing to the presence in the vapor of inert, non-condensable gases; if these are large in amount the pressure will rise greatly. Provision must be made for taking these out of the condenser, either with the condensed liquid or separately. Obviously the heat of condensation evolved in the condenser must be removed by absorption, as otherwise condensation of the vapor will be incomplete, the pressure will rise and vaporization in the evaporator will be retarded. This requires adequate condensing surface and cooling medium.

Condensers.—The condenser may be of two types: (*a*) the cooling water is kept separate from the condensing vapor (*surface condenser*) and (*b*) it mixes directly with the vapor as a spray or film (*jet condenser*).

In *surface condensers*, to secure a high overall coefficient of heat transfer from condensing vapor to cooling medium, the requirements[2] are, rapid circulation of the cooling medium to reduce the effective thickness of water film through which heat must flow by conduction, immediate removal of the condensed liquid, and as complete removal as possible of non-condensable

[1] To make negligible any drop in pressure from point to point due to friction of the flow of vapor.

[2] See pp. 134 to 158.

gases to prevent the formation of an insulating film of relatively stationary gas.

The advantages of the *surface condenser* are, that the condensate is obtained uncontaminated with the cooling water, that the capacity may be varied widely by controlling the rate of flow of the cooling water, and the cooling water does not have to be pumped out of the vacuum.

The advantages of a *jet condenser* are, that very rapid transfer of heat and hence large capacity per unit floor space is obtained because of the direct mixing of vapor and cooling water, relatively simple construction at a low cost, and the fact that corrosive vapors

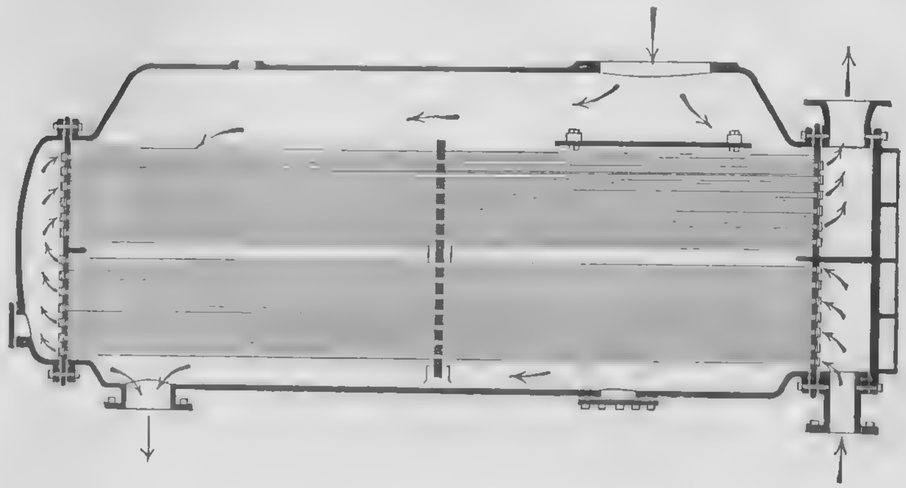


FIG. 92A.—Wheeler Surface Condenser.

may be condensed without destruction of the containing walls or the use of specially resistant material.

The disadvantages of the *jet condenser* are, the larger volume of cooling water required, the necessity of lifting all the cooling water as well as the condensate and fixed gases from the prevailing vacuum to atmospheric pressure, and the unavoidable escape of the permanent gases dissolved in the cooling water into the vapor space with corresponding rise in pressure.

In both types of condensers the liquid and gases may be removed by a wet-air pump, or separately by a dry-air and a liquor pump. When a barometric leg is employed no pumps are neces-

sary,[1] but the vacuum is improved by the use of a dry air pump connected to the top of the apparatus.

Heating Elements.—The small area of heating surface furnished by a jacket, makes such an apparatus undesirable for rapid evaporation of large volumes. Recourse is had therefore to heating elements made from pipe, either in the shape of coils, which may be of most complex forms, or straight pipe set in tube sheets at either end. The factors in the design of the heating surface have been outlined, and will be further discussed in connection with the various types of steam-heated evaporators.

Frothing and Entrainment.—Since the object of evaporation is the separation of vapor from residue, it is essential to secure such separation before the vapor passes to the condenser.

In rapidly boiling liquids, the escaping vapor has a strong tendency to carry liquid with it, sometimes as bubbles or froth, and sometimes as suspended droplets, probably produced by the bursting of bubbles during the escape of the enclosed vapor. The former is called *frothing*, and the latter *entrainment.*

Frothing.[2]—With badly frothing liquids, where the bubbles are stable and persistent, it is sometimes difficult to prevent almost the whole body of liquid from lifting over with the vapor. Usually, however, the bubbles can be broken up by passing the froth over additional heating surface; this causes further evaporation, with resulting distention of the bubbles to the point where they burst. This is readily accomplished where the heating surface is in the form of coils or closely packed tubes, but the heating elements must be well distributed through the path of the frothy vapor, as the conductivity of such a mass is poor. In practice, if the liquid in such an evaporator begins to froth, the liquid level is lowered until a portion of the heating surface previously submerged is exposed to the vapor, thus lessening the amount of vapor disengaged below the surface of the main liquid mass and allowing the froth produced to play over the heating surface above the liquid, the level being so adjusted that the froth is broken up just at or above the top of the heating surface. Otherwise any heating surface in contact with vapor alone would be ineffective in evaporation. The proper location of the level between main liquid and froth is determined by experiment. The lowering of liquid level to reduce foaming has the disadvantage of the formation of scale on the heating surface; where this deposited matter does not dissolve readily, the disadvantage is serious. Foaming liquids can also be treated in film type evaporators (see pp. 410 to 415).

[1] Although in a barometric condenser, that is, one so placed that the cooling water and condensate flow by gravity through a column of liquid equivalent to the prevailing vacuum, no pump is required, yet this quantity of cooling water must at some time have been pumped to the top of the condenser, and an equivalent amount of energy expended.

[2] DAUBE, *M. I. T. Thesis, 1919*, found that the height of foam produced by bubbling air through a soda-ash solution was directly proportional to the average depth at which the bubbles were formed, and proportional to approximately the 0.8 power of the linear velocity of the gas. For a given apparatus, liquid, and liquid depth, the height of foam produced at a definite linear gas velocity was practically the same under atmospheric pressure or vacuum, and whether hydrogen, air, or carbon dioxide was used. These experiments indicate that it is linear velocity, and not mass velocity, that determines foam formation. Since the shape of the evaporator and the physical characteristics of the liquid in question have a profound influence on the foam formation, experimental work should be done in each case to determine the foaming characteristics.

Entrainment.—It seems probable that the most important factor in determining entrainment is the "mass velocity" of the vapor rising from the free or disengaging surface of the liquid in the evaporator, *i.e.*, the pounds of vapor escaping through each square foot of disengaging surface per hour. The disengaging velocity allowable must, however, be determined for each specific case, as the viscosity, density, and surface tension of the liquid affect the result. Since the first and last of these vary greatly with change in temperature, hence with change in pressure, and also with concentration, it is unsafe to determine the maximum allowable disengaging velocity at other than the actual conditions to be encountered in the evaporator. A determination made experimentally in a small apparatus will, however, enable one to estimate within reasonable limits the conditions that will be encountered in practice.

To allow such particles to settle back into the evaporator, it is important to provide above the disengaging surface of the evaporator reasonable headroom in which there is no constriction of area of cross-section, thus avoiding increase in the velocity of the rising vapor. In industrial apparatus, this headroom is rarely less than 30 in., and should be 6 to 15 ft. The disadvantages of increasing headroom come from the increased size

of the apparatus and the greater heat loss to the surroundings. Owing to the small ratio of external surface to volume in large evaporators, it is possible in such to increase the height of the vapor space without increase in percentage heat loss beyond what would be found in a small evaporator.

It is found advisable to remove the droplets which remain in the vapor by utilizing centrifugal force. This is accomplished by passing the vapor through a vessel of greatly restricted section having a circular path, with provision for draining back into the evaporator the particles impinging upon the walls. Where appreciable decrease in pressure of the vapor is allowable, it is possible to produce a high velocity through a long path, against baffle plates, and thus secure very effective removal of drops. The passage of the vapor around and against baffles followed by temporary reduction in velocity is sometimes used to separate discrete particles therefrom, but the major action is the centrifugal effect at the points of change in direction. (See Fig. 94, p. 410.)

Energy Required for Evaporation.—The measure of the theoretical difficulty of carrying out any reaction or separation is the minimum amount of work necessary to effect the change involved, if performed under theoretically perfect and reversible conditions, *i.e.*, the change in free energy. A process should be able to operate with a work consumption not greatly exceeding this value. It should be remembered that this energy must be supplied as work; mere heat is not its equivalent, though for convenience the energy is often expressed in heat units. On pp. 439 to 440 equations are given for the minimum amount of work required, and it is shown that this is very small, amounting, in the case of a 10 per cent water solution of glycerine, to but 6.4 B.t.u. per lb. of water evaporated. It is evident that the more concentrated the solution the greater is the theoretical energy required, but even for concentrated solutions, this value remains small. For colloidal solutions, *i.e.*, those of high molecular weight, the reversible work is even less. Theoretically, therefore, the greater part of the heat supplied in evaporation should be recoverable, and such is the case.

It was emphasized that the free energy necessary was a work and not a mere heat requirement, but since available heat engines actually convert 20 per cent, or more, of the heat supplied into work, the theoretical *heat* requirement for a 10 per cent glycerine

solution is only 32 B.t.u. per lb. of water evaporated. From this point of view, a simple evaporator is a very inefficient mechanism. However, the heat required for evaporation is almost entirely converted into latent heat of vaporization, and is, in this form, carried out of the evaporator by the vapor and can be again utilized by condensing the vapor.

Suppose, for example, that in a given plant a certain amount of water is being evaporated at atmospheric pressure in the process of concentration of an aqueous solution. Most of the heat consumed appears as latent heat in the water vapor. It could not, however, readily and directly be employed to evaporate more water under these conditions, since on condensing it this heat is evolved at the boiling point (100° C.), so that no temperature difference exists to force the heat through the necessary heating surface into the fresh solution to be evaporated. If, however, the same plant had a corresponding supply of alcohol to be distilled, the water vapor from the above evaporator could readily be used as a heat supply therefor, by condensation in the heating coils of the alcohol still, rather than using boiler steam for this still. If, in turn, this same plant had ether to be distilled, the heating coils of the ether still could be used as a condenser for the alcohol vapor, thus avoiding the use of boiler steam in the ether still. In this way a succession of liquids of progressively lower boiling points can be evaporated with a single supply of heat. In other words, in the process of evaporation, the heat used is merely degraded in temperature and this degradation is slight.

Multiple Effect Principle.—However, the conditions above outlined which allow a given quantity of heat to be used for evaporation a multiple of times by boiling a series of liquids of successively lower boiling points do not frequently exist. But it is true that the boiling point of a water solution depends upon the pressure above it, and by a judicious selection of pressures, a solution can be made to boil at the temperatures given for alcohol and ether or any more suitable temperatures, and a similar economy of heat effected. Each evaporator (kettle or pan) is called an "effect" and this process is called *Multiple Effect Evaporation.*

Suppose, for example, the steam entering the coils of Effect *A* in Fig. 93 is saturated exhaust steam at 4.2 lbs. gauge (18.9 lbs. per sq. in. abs. pressure) and at 225° F., and the pressure in the

vapor[1] space of A corresponds to a vacuum of 8.75 in. of mercury, or with normal barometer 10.4 lbs. per sq. in. absolute pressure. The water in A will boil[2] at 195° F., and furnish steam to the heating coils of B at this temperature. The vacuum in the vapor space of B is 19.1 in. and hence water will boil at 165°. The vapor coming from B and entering the heating coils of C at 165° will cause water to boil in C at 125° where the vacuum is 25.9 in. Vapor from C at 125° will then pass to the condenser.

Since the heating element of A is above atmospheric pressure, the condensed water in it can flow from it by gravity at a

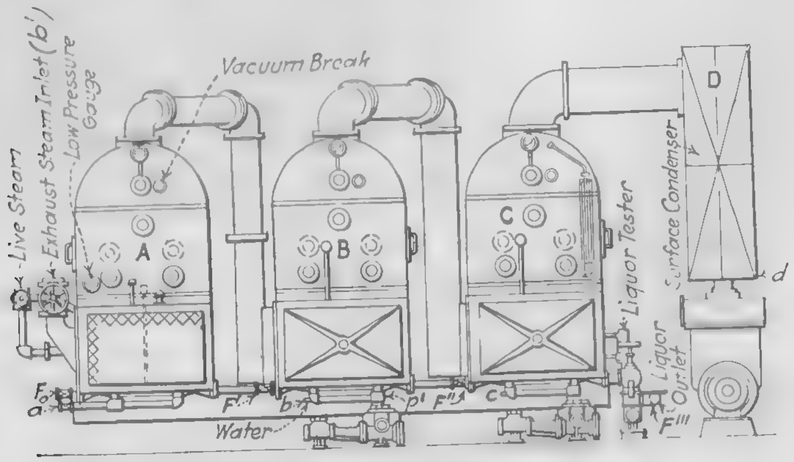


FIG. 93.—Multiple Effect System (Swenson).

little below 225° F. But the condensed water in the heating space of B is under vacuum, hence the pump P' must be used to exhaust the heating space in B and deliver the water at atmospheric pressure. Similarly, the condensate in the heating space of C and the surface condenser D must be pumped out.

It is evident that the condensed water from the heater in A at about 225° is in position to give up part of its sensible heat to the liquid boiling in B at 165°, and by leading it into the heating element of B part of it flashes into steam on account of the lower

[1] For the sake of clearness the steam evolved by a boiling solution will be referred to as "vapor" while the word "steam" will be used to designate the source of heat in any particular effect. Obviously the vapor from one effect becomes the steam supply of the next.

[2] For the purpose of simplicity, in this illustration boiling point raising has been neglected.

pressure, reducing its temperature to 195°, the temperature of the steam in the coils of B. Similarly, heat may be recovered from the condensate from the heating surface of B, by passing it into the coils of C.

The solution to be evaporated is fed at 195° into the liquor spaces of Effect A at F_a by means of a pump, or by gravity. Since the pressures in B and C are progressively lower, it is evident that the solution can be drawn in sequence through the system by the pipes F' and F'' and finally lifted to atmospheric pressure by the pump F'''. This arrangement is called "*parallel flow*," since the vapors and liquors flow in the *same* direction. In order to insure the absence of fixed gases in the heating space of all the effects, each is connected by a small pipe to the vacuum pump or to the body of the vapor space of the same effect which is obviously at lower pressure. Where the non-condensable gas is small in amount the latter is better practice, as this method acts as a safeguard against the loss of steam due to its discharge with fixed gases.

Economy Versus Capacity.—Theoretically, therefore, in this case one pound of initial steam should evaporate approximately one pound of water in each of the Effects A, B, and C. In practice, for reasons discussed later, the evaporation per pound of initial steam, even for a fixed number of effects operated in series, varies widely with conditions, and is best predicted by a "heat balance." The *heat economy* of such a system must not be confused with the *evaporative capacity* of one of the effects. If operated with steam in the heating space of 225° and 25.9 in. vacuum in its vapor space, Effect A will evaporate as much water (nearly) as all three effects costing more than twice as much; but it will require approximately three times as much steam and cooling water. The capacity of one or more effects in series is directly proportional to the effective temperature difference between temperature of the steam supplied and the temperature of the boiling solution in the last effect. Hence if this remains constant, the capacity of one effect is the same as a combination of three effects. On account of complications in construction and operation of multiple effects, they are not so frequently used for the evaporation of corrosive liquids, or where fuel is very cheap, or for small scale processes, but they are of great value and importance in increasing the economy of large scale evaporative proc-

esses, and are continually being simplified and improved. The savings resulting from the installation of additional effects are discussed on pp. 424 to 427.

Efficiency Versus Economy.—In this connection, it may be noted that, in the literature on evaporators, the word "efficiency" is often erroneously used for the "capacity" of a system. The true efficiency of any evaporative system can be determined, as shown on pp. 402 to 403, but since the data for this are frequently inadequate and almost always inexact, it is wiser to express the performance of a given apparatus as its heat "economy," *i.e.*, the evaporation obtained per unit of steam consumption. This removes any uncertainty in the expression of the result.

Terminal Conditions.—The highest temperature employed in an effect is limited by the corresponding pressure, which must not exceed the working strength of the apparatus. At times it is of course limited by the pressure of the available steam supply;[1] also, by the temperature to which the solution may be safely heated. The lowest pressure which can be realized depends upon the temperature of the cooling water. These limiting temperatures, together with the nature of the solution to be evaporated, and the product required, are factors not usually within the control of the designer of evaporative equipment, but are already determined. Collectively, they are designated the "terminal conditions" of an evaporative system, and represent the fixed and accepted limitations under which the equipment must be designed to operate.

Theoretical Limit of Number of Effects; Boiling Point Raising.—Every solution exerts a vapor pressure less than that of the pure solvent at the same temperature, and corresponding to this vapor pressure lowering is an equivalent boiling point raising. That is, dissolved substances lower the vapor pressure of the solvent, such reduction increasing with the concentration of solute. Since a solution boils when its vapor pressure reaches that of its surroundings, it must be heated to a temperature above the boiling point of the pure solvent, before ebullition can take place. The vapor rising from a solution is therefore superheated

[1] Where power is needed in the plant boiler steam may be expanded down to nearly atmospheric pressure through turbines or steam engines, the exhaust steam being used for the evaporators. However, see p. 427.

by an amount exactly equal to this boiling point raising (b.p.r.) and it must be cooled by this amount before it will condense and give up its heat of vaporization. While the amount of superheat is small when compared to the latent heat of the vapor, it should be noted that this latent heat of vaporization becomes available for use only when cooled to a temperature lower than the solution from which it came by the amount of this b.p.r. This loss of temperature difference from condensing steam to boiling liquid in the next effect increases the heating surface required for the transfer of the heat. As is shown on page 432, a 33.3 per cent caustic soda solution has a b.p.r. of 34° F. Theoretically, the temperature gradient from one effect to the next may be changed at will, but the drop due to the b.p.r. is a fixed quantity for any determined concentration of the solution. The possible number of effects, therefore, is limited to the total temperature drop available to force heat through the heating surface (and this is the difference in temperature between the steam supply and the cooling water) less the total b.p.r. in all effects. This subject will be further discussed on pp. 428 to 429.

Multiple Use of Steam Through Mechanical Work.—In the above discussion, the point was made that work, rather than heat, is the essential thing in evaporation, and yet the methods of evaporation presented have involved heat transfer alone. It is, however, possible to use mechanical work effectively in evaporation, by mechanically compressing the vapor given off from an evaporating solution (more or less superheated by the b.p.r.), and again using the high-pressure steam thus secured, in the steam coils of the same effect from which the vapor came.

As was stated on page 403, the only reason why the vapor coming from Effect *A* could not again be used in *A* to evaporate more solution, is that it is at the same temperature as the solution boiling in *A*, and hence the heat would not flow from the heating space through the container walls into the solution. The heat units are present in the vapor as latent heat, but they are available at too low a temperature and pressure. If now, this vapor be compressed to the proper pressure, its condensation temperature will be so raised as to be again available for transferring heat in the heating coils of Effect *A*. The chief difficulty with such a process lies in compressing large quantities of low-pressure vapor,

having a large volume, from the saturation point up to a pressure high enough for use in the heating coils. Due to cooling by radiation, and to entrainment, it is impractical to use an ordinary air compressor; the erosion of the mechanical parts is also a disadvantage. The only method, heretofore adopted for overcoming this, has been the use of a steam ejector, employing high-pressure boiler steam to draw the vapor out of the evaporator and compress it to the degree required. The resulting mixture of steam from the evaporator and the boiler then flows to the steam coils of the evaporator itself. The condensation there obviously leaves an excess of uncondensed steam, which goes to a feed-water heater or to waste. With this system, it is possible to evaporate about three pounds of water per pound of boiler steam, or the equivalent of a triple-effect evaporator; but with high compressive efficiency and small heat losses, it should be possible to evaporate much more water per pound of boiler steam than this. The development of this type of mechanical evaporator offers much promise, especially, for use where power is cheap relative to fuel. In its present form, this evaporator should be considered for small installations, as it makes possible the realization of high heat economy in a single effect.

TYPICAL EVAPORATOR BODIES

In any evaporator effect, there must be provided (1) means for supplying steam to the heating surface, (2) means for removing the condensed water and non-condensable gases, (3) disengaging space for separation of vapor from boiling liquid, (4) means for admission and removal of the liquid to be concentrated, and (5) provision for removal of vapor evolved.

The heating surface of an effect is generally made up of tubes, straight on account of ease of construction and cleaning, either horizontal or vertical, or inclined at an angle. The boiling liquid may be either outside or inside these tubes, the steam being in either case in contact with the other surface. And finally, the boiling liquid may lie over the heating surface as a deep layer, *i.e.*, the tubes submerged in the liquid, or the boiling liquid may be distributed over the heating surface as a thin film. Corresponding to these possibilities, evaporator effects may be classified under the following types:

Tubes horizontal	Liquor *outside* tubes	Submerged Tube Type	(1)
		Film Type	(2)
	Liquor *inside* tubes	Submerged Tube Type	(3)
		Film Type	(4)
Tubes vertical (also inclined)	Liquor *outside* tubes	Submerged Tube Type	(5)
		Film Type	(6)
	Liquor *inside* tubes	Submerged Tube Type	(7)
		Film Type	(8)

Effects, corresponding to all but one of these types, are found in commercial operation. Formerly there were several types known by the names of their designers, but experience has standardized practice in construction, and a few types are now accepted as having justified themselves, and can be obtained of any one of a number of manufacturers.

Type 1. Tubes Horizontal, Liquor Outside, Submerged Heating Surface.—This is an important and widely used type. In the evaporator shown in Fig. 94, the steam is supplied to one of the two steam chests, from which it is distributed to the steam tubes, and the condensed steam is trapped out from the bottom of the chest at the other end of the tubes. The boiling liquid is in the main body of the evaporator around the heating tubes, and the space above the liquid serves for settling the entrained droplets from the vapor. The dilute liquor is fed in through a supply pipe at one side of the evaporator either above or below the liquor level, sometimes through jets, and the more concentrated liquor flows out at the bottom of the opposite side. The vapor leaving the top of the disengaging space, before entering the vapor main leading to the next effect or to the condenser may pass through a steam separator (" catch-all ") containing one or more baffles for further separation of the entrained liquor from the vapors. The steam tubes are fitted into the steam chest with gaskets of rubber or other suitable packing material, held tight by face plates screwed down upon the gaskets from the steam chest side. In order to insure circulation of the boiling liquid, a space, entirely free from tubes is provided, either at the center or at the sides or both. Evaporators of this type are constructed by practically all manu-

facturers. For example, the Swenson horizontal tube evaporator (Fig. 93) has a rectangular body, while the Zaremba (Fig. 94) has a vertical cylindrical body. The differences in evaporators of this type supplied by the various companies lie mainly in the effectiveness of maintaining circulation and in simplicity,

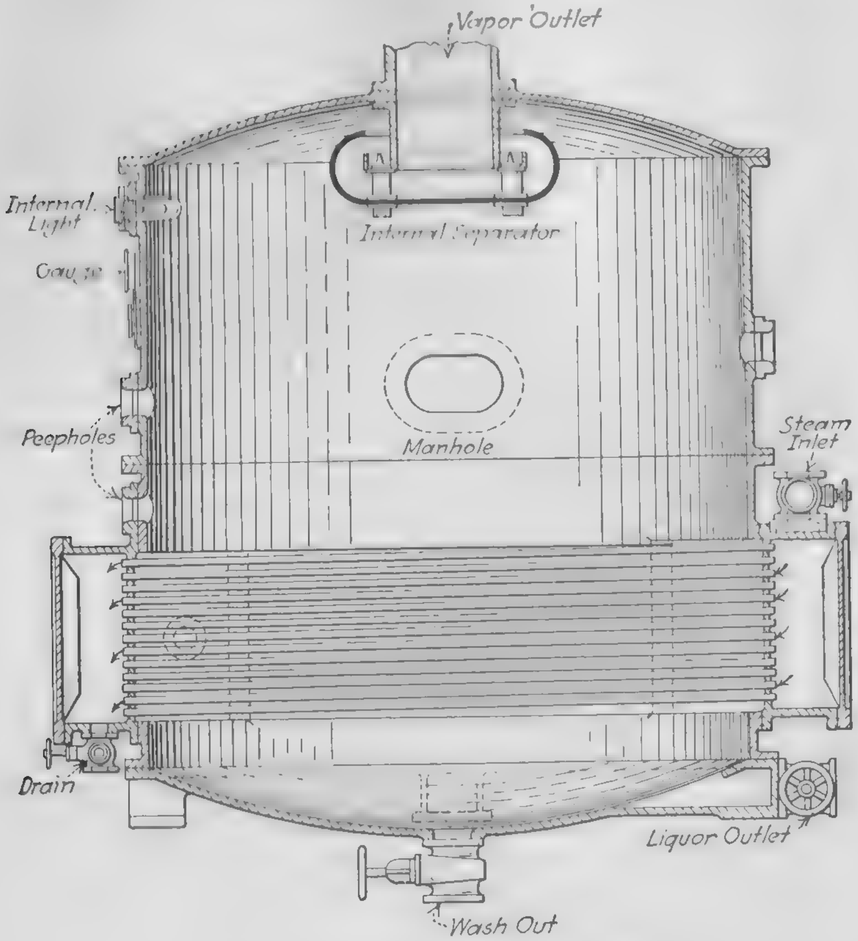


FIG. 94.—Evaporator, Type 1 (*Zaremba*).

strength and perfection of mechanical construction. The relative location and size of heating surface and free circulation space have a large influence in determining the rate of circulation, and therefore the coefficient of heat transfer.

Type 2. Tubes Horizontal, Liquor Outside in Film Form.—The Lillie evaporator is the only modern representative of this

class. In this type there is only one steam chest and each of the parallel tubes containing the steam is closed at the extreme end except for a small opening which allows the non-condensable gases to escape into the disengaging chamber which surrounds the tubes. The tubes slope slightly toward the steam chest to drain out the condensed water which is trapped out from the bottom of the chest. The feed liquor is distributed over the top rows of steam tubes through a suitable distributing device, usually consisting of parallel perforated pipes or troughs. The concentrated liquor collecting in the bottom of the disengaging space is pumped out, and is either recirculated through the same effect, distributed into the next effect in series with the first, or withdrawn as product.

It has been shown that if an evaporating liquid begins to froth, it is possible to stop this by lowering the liquid level, so that the liquid plays over the heating surface as a foam. Evaporators of Type 1 when used with frothing liquids, are operated in this way and should then be classified as Type 2.

Type 3. Tubes Horizontal, Liquor Inside, Submerged Heating Surface.—This type has never been realized owing to the impossibility of removing vapor from the tubes without at the same time carrying out the liquid. The nearest analogue is the water-tube boiler, but in this case, the heating element is not steam.

Type 4. Tubes Horizontal, Liquor Inside in Film Form.—The Yaryan evaporator (Fig. 95) is equipped with horizontal tubes surrounded by steam. The feed liquor enters the tubes and flows through several horizontal passes, leaving at the opposite end to discharge into the disengaging chamber, in which the entrained liquor is separated from the vapor by suitable baffles. The liquid in the tubes flashes partly into vapor and rushes through the tubes as a froth consisting of alternate slugs of vapor and boiling liquid. The concentrated liquor is drawn off while the vapor passes to the steam space of the next effect in series, or to the condenser. The high velocity of liquid induced by the evaporation in the first part of the liquid path gives a very high coefficient of heat transfer, but in the last part of the path although the velocity is still higher, the material flowing is largely vapor and hence the coefficient of heat transfer is low. The net result is that the average coefficient of heat

transfer for the entire path is usually somewhat lower than is realized in other types. It is obvious that the total amount of liquid exposed to high temperature is small compared to the amount so exposed in Type 1, and hence the *time of exposure* of liquid to the high temperature is much less. Therefore for materials which deteriorate on long heating, the use of an apparatus of this type is desirable. Other types of evaporators in which the time of exposure is short will be discussed later.

Type 5. Tubes Vertical, Liquor Outside, Submerged Heating Surface.—In the earlier days of evaporator practice, effects were constructed of large vertical cylindrical shells, the heating

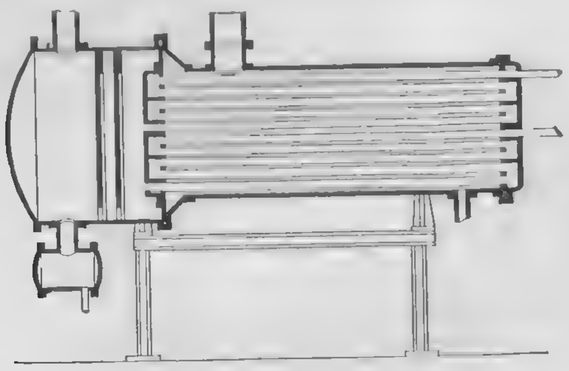


FIG. 95.—Evaporator, Type 4 (*Yaryan*).

elements consisting of vertical steam tubes connected at top and bottom into horizontal headers for supply of steam and removal of condensate. Such effects were at one time spoken of as the "standard"[1] type. It is, however, difficult to insert such heating elements, so as to secure a maximum heating area in a given volume of the body of the effect; and, moreover, the steam headers interfere with the circulation of the boiling liquid, thus cutting down the heat transfer coefficient. The use of this type has in general been abandoned.

Type 6. Tubes Vertical, Liquor Outside in Film Form.—The type described in the preceding paragraph, when used for frothing liquids, employing the method previously mentioned of lowering

[1] This term is now applied to Type 7 with central downtake.

the level of the boiling liquid so that the major portion of the heating surface is covered only with the foam and bubbles produced by ebullition, falls under this head. Since it suffers from all the disadvantages of the construction using submerged heating surface, it is no longer used.

Type 7. Tubes Vertical, Liquor Inside, Submerged Heating Surface.—This important evaporator type is usually built of a vertical, cylindrical shell with, however, two available methods of insertion of the heating tubes. The ends of these may be expanded into plates or "diaphragms" extending clear across the evaporator body, and thus forming a suitable steam chest; in the center a large circular tube is provided for descent of the liquor, which rises through the heating tubes.

Frequently the steam chest consists of a short cylindrical shell, somewhat smaller than that of the evaporator itself, closed at the ends by tube sheets into which closely spaced heating tubes are expanded. This steam chest is supported concentrically within the main evaporator shell. From the shape of the steam chest, it is described as a "basket." In the case of single effect finishing pans, such as "strike" pans for sugar, a central downtake is sometimes provided.

The notable advantage of Type 7 is the ease of cleaning the heating tubes from incrusted matter by running a rotary cutting tube-cleaner through the tubes. To this end, the diaphragm type is provided with man-holes, while the main body of a "basket" effect (Fig. 96) is flanged, so that the whole basket can be removed; extra baskets are usually kept on hand so that operation may be quickly resumed, and the incrusted basket cleaned or repaired at leisure.

Salt solutions often contain gypsum, marked in its tendency to form a dense, adherent scale of such low heat conductivity that the evaporative capacity of the apparatus is rapidly reduced. This type is well suited for use in concentrating such solutions, and is so widely used for this purpose that these effects are frequently termed "salt evaporators."

Type 8. Tubes Vertical, Liquor Inside in Film Form.—Evaporators of this type consist of a group of long, vertical tubes, the ends of which are expanded into two plates which form diaphragms across a cylindrical shell near the ends, the space

between these plates being the steam chest. The liquor is fed into the shell below the bottom plate, under sufficient head to rise a short distance into the tubes. There it boils, and the vapor rising

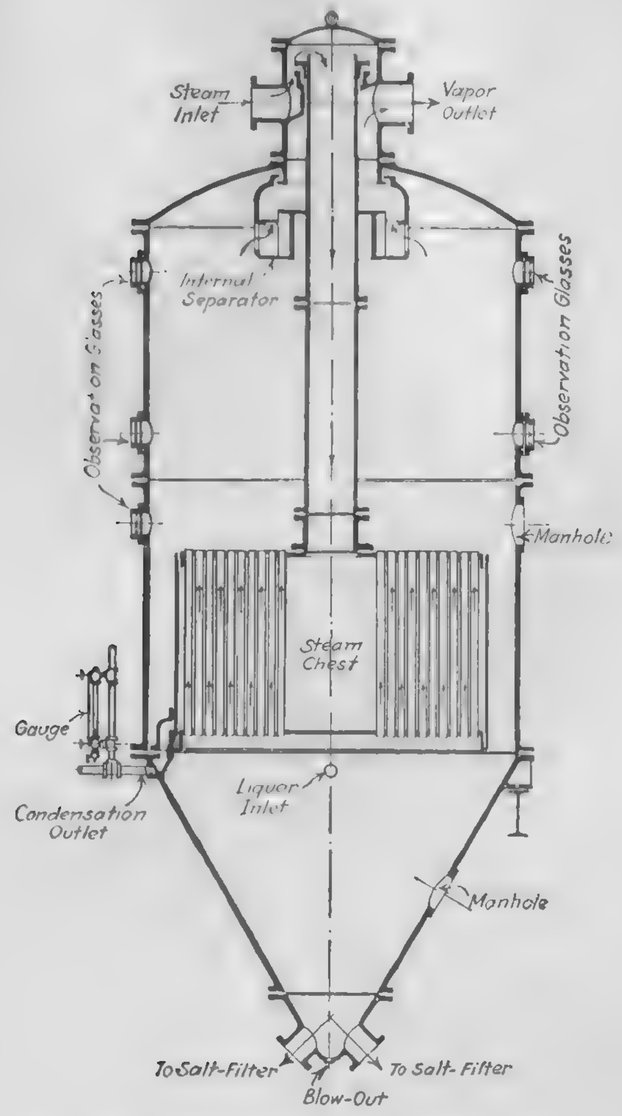


FIG. 96.[1]—Evaporator, Type 7 (*Basket Type*).

as froth forces slugs of liquor ahead of it at high velocity up the tubes and out into the disengaging space in the evaporator shell above the upper tube plate. In the Kestner (Fig. 97) the dis-

[1] *Courtesy of Buffalo Foundry & Machine Co., Buffalo, N. Y.*

engaging space is, however, so small that a centrifugal separator is used. The liquid, after passing through the tubes and separating from the vapor, is led down through a return pipe from which it can be deflected either back to the bottom of the evaporator shell for recirculation, or to a second effect, or drawn off as product.

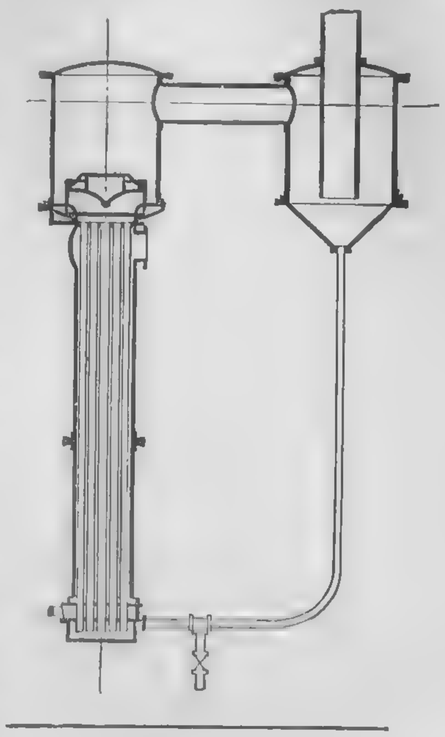


FIG. 97.—Evaporator, Type 8 (*Kestner*).

The distinctive advantage of this type lies in the high heat conductivity realized, due to the great velocity of the liquid over the heating surface. The character of the flow of liquid and vapor through the tubes guarantees a thorough and rapidly repeated wetting of the whole heating surface. Unlike the Lillie, the velocity is high because the flow is forced—not due to gravity alone. This type has interesting possibilities, and its features should be carefully studied to secure further development in design.

Evaporators of Type 8 are sometimes built with inclined tubes, thus reducing the head room required.

Evaporators of Type 7 when used for the concentration of frothing liquids are operated by lowering the liquid level (see p. 400). They thus become in effect Type 8 evaporators.

Salting-out Evaporators.—Evaporator bodies which are to be used for solutions depositing crystals during the process of concentration must have provision for removal of the crystals. Since interference with continuity of operation is very undesirable, the evaporator is equipped with a type of double seal, known as a "salt catch." This consists of a chamber separated from the evaporator just above it by a gate valve and in the bottom of which is a second such valve. The bottom of the evaporator body is

sloped downward, as in Fig. 96, p. 414, to the upper valve, so that crystals deposited will fall upon it, and flow through it when opened. Sometimes the salt receiver is fitted with a filter plate, so that when full the mother liquor may be drawn off, and the crystals washed. They may then be dried, first by passing dry steam and then air through them. Or, as in the separation of salt from electrolytic caustic soda solution, the salt, after being washed, is dissolved in hot water and pumped or forced out.

NOTES ON SINGLE EFFECT EVAPORATORS

As already shown, to maintain a low temperature, the evaporation of liquids liable to injury by heat is conducted at the highest available vacuum. Since only the last effect of a multiple evaporator system can be under the highest vacuum and therefore at the lowest temperature, this type of apparatus does not lend itself to the concentration of liquids injured by heat except when the same are very *dilute;* for example, solutions of sugar, glue, tannin, etc. Injury due to "burning" occasioned by localized lack of circulation with resultant overheating is decreased by using a lower steam pressure and a correspondingly larger heating surface. Obviously where the material in solution is sensitive to heat it is desirable to hold it at the temperature of the evaporator as short a time as possible. Since a film type of evaporator contains the minimum of liquid at any given time it is from this point of view particularly desirable. Unfortunately, however, in an apparatus of this type intermittent wetting and drying of the heating surface is very likely to take place and in the case of glue or similar substances an adherent insulating film forms on the heating element when dry which does not readily re-dissolve when again wet. The vertical tube type, however, is much less subject to this drawback and should find here a promising field for development.

Another advantage of film-type effects for handling liquids injured by heat is the absence of any boiling point raising due to hydrostatic head. With submerged heating surface, the liquid at the bottom of the pan is under a pressure greater than that at the disengaging surface above, by an amount equal to the liquid head in the effect, which may be several feet. At high pressures, this additional head is negligible, but at very low pressures the

increase will cause a marked rise in temperature at the bottom of the pan. It is true that the liquid at the bottom of such an effect often does not boil, but is none the less raised in temperature and is then brought by convection up to the surface where, being super-heated, it flashes partially into vapor, while the residual liquid, cooled by this evaporation, then returns to the bottom of the effect to repeat the cycle. Thus in any case, hydrostatic head produces an increase in the average temperature of the boiling liquid (marked when operating under high vacuum) which can be avoided by film evaporation.

In the refining of sugar it is essential to regulate the number of crystallization centers formed and the rate of growth of the resultant grains, by controlling (1) the concentration of the solution, (2) its temperature, (3) the rate at which it is brought to any definite temperature and pressure, (4) the rate of cooling and (5) the extent of cooling to which it is finally subjected. The first three of these factors are determined entirely, and the last two to a certain degree, by careful manipulation of both heat supply and vacuum in the evaporator. For this purpose a single effect must be used, as the reaction of one effect upon the operation of another in series with it would render close control impossible.

Single effects are used, as already indicated, in small installations, where the amount of evaporation to be done is insufficient to justify the cost of installing and operating a multiple effect system. (See pp. 405 to 406.) Single effects are also used in many cases where it is desired to recover the solvent employed, but where otherwise an open pan could as easily be used.

It is desirable to bring together, even with danger of reiteration, the more essential details for which it is necessary to provide in order to secure satisfactory operation of evaporators. These requirements must be met in every effect, whether operated separately or in series with others; the modifications of these directions necessary in series operation will be pointed out in the discussion of multiple effects.

Steam Supply.—The steam feed of an effect should be through pipes large enough to insure no *appreciable* reduction in pressure caused by friction in the supply lines and valves (a point of great importance when using low-pressure steam), and should be drawn from an adequate source to insure the maintenance of full pressure in the steam chest at all times. Where the original supply

is from a boiler or other source in which the pressure is too high for the safety of the apparatus, it is imperative that the supply line be equipped with a proper automatic reducing valve, to protect the effect and yet to insure, at all times, full working pressure on it. In this last case, a safety valve should also be provided.

Removal of Condensed Steam.—Provision for this is of utmost importance. The heating tubes must not be too long (preferably not over 70 diameters for horizontal tubes) as otherwise the down-stream end may fill with condensed steam, rendering that portion of the heating surface useless. A maximum value is 150 diameters. Where possible, the tubes should slope in the direction of flow of the steam in order to effectively sweep out the condensate. The condensed steam chest must be equipped with an effective trap to remove condensate as soon as accumulated, without allowing escape of steam. The removal of the non-condensable gases always present in the steam is of great importance, as otherwise these gases will accumulate and entirely prevent the entrance of the steam. This removal is effected by bleeding off a part of the steam from the highest point in the condensed steam chest, to the vapor space of the same effect or directly to the condenser. The ideal system involves a relatively high steam velocity through the heating surface, sweeping the gases immediately into the condensed steam chest, from which they are removed.

A gauge glass should be provided to detect inadequate removal of condensed steam from the steam chest. The presence of non-condensable gases is detected by the discrepancy between the temperature in the steam chest and the pressure existing there.

Entrainment in an effect is indicated by the presence of solute in the condensed vapor. *Frothing* is detected by inspection through sight glasses in the side of the effect, or by watching gauge glasses connected at various heights in the side of the pan and leading thence to any point of low pressure, such as the condenser, or a succeeding effect. By the use of electrical contacts in a gauge glass, or at definite heights in the disengaging space of the effect, an alarm may be given in the case of solutions of electrolytes. Frothing is reduced by lowering the liquid level in the effect, or by reducing the evaporative rate.

Liquor Feed and Removal.—By proper control of the feed, a single effect may be operated either intermittently or continuously. The body of the effect is filled to the proper height with dilute liquor, and as concentration proceeds the level is maintained by admitting more dilute liquor at the proper rate, until ultimately the required concentration is realized; then the effect is emptied, and the cycle repeated. Or, instead of emptying the effect when the desired concentration is attained, the concentrated liquor may be drawn off at a definite, constant rate, determined by the evaporative capacity of the effect, the liquor level being maintained uniform by the continued admission of dilute liquor, thus securing continuity of operation. Discontinuous operation requires constant attention to control the changing rate of evaporation consequent upon decreasing temperature drop (and hence decreasing heat flow) through the heating surface caused by the constantly rising boiling point of the solution, and to provide for emptying and refilling the effect. Hence, continuous operation is generally used. This involves the disadvantage that the entire evaporation is carried out at the high boiling point of the concentrated solution, the *average* boiling point raising of discontinuous evaporation being much lower. In multiple-effect operation, on the other hand, this disadvantage largely disappears, as will develop later.

The liquor feed of an effect is controlled by a valve operated either by hand or automatically (as with a float valve) so as to keep the amount of boiling liquid in the effect at the proper level. Film type effects usually require delivery of the feed at special points, as indicated in their description; but in the case of submerged heating surface, the liquor may be admitted anywhere, as boiling keeps the contents of the effect thoroughly mixed. The concentrated liquor is removed at a point some distance from the inlet, to prevent short-circuiting of the dilute feed-liquor to the outlet pipe, and its flow is controlled by a throttle valve, operated to maintain the proper concentration of the effluent, usually determined by its gravity. The feed to effects under pressure and the discharge from those under vacuum must be by means of suitable pumps. The operator observes the amount of liquor in the effect through sight or gauge glasses.

Vapor Removal.—The vapor is removed by a condenser, which, if operating under a vacuum, is fitted with an air pump. These two pieces of apparatus are of the types used in steam engineering practice, and their operation involves nothing unfamiliar. Jet

condensers are used in a larger proportion of the cases in chemical practice than in steam engineering, owing to less trouble from corrosion. The air pumps must be adequate for removal of all inert, non-condensable gases present. Barometric jet condensers are used in many cases where corrosive gases enter with the steam. While this type avoids corrosion of pump parts, its height limits its use where space considerations are involved.

CHARACTERISTICS OF MULTIPLE EFFECT SYSTEMS

It may at first thought seem that the maintenance of the proper conditions of temperature and pressure in each of the various bodies of a multiple effect system is a difficult and complicated problem, but since the adjustment of conditions between the pans is entirely automatic, such is not the case. When a number of effects are to be operated in series, the vapor from the first discharges into the steam coils of the second, the vapor from the second passes into the steam coils of the third, and so on; the vapor from the last effect passes directly to the condenser. In such a system the liquor feed and discharge of each body may be entirely separate, as though each were a single effect; however, this is seldom done.

Parallel Flow of Liquor and Steam.—It is advisable, however, to feed the dilute liquor to the first high-pressure effect, carrying on only a part of the concentration there, feeding the second effect from the first, the third from the second, and so on, finally withdrawing the concentrated product from the last effect. There are two reasons for this. First, only two liquor pumps are required, the feed pump to the first effect (if it be under pressure), and the discharge pump from the last, since as each is at a pressure lower than the preceding one, the liquor will flow directly from effect to effect. Second, since all effects before the last contain liquor which is but partly concentrated, the b.p.r. in these effects is correspondingly lower, thus giving a larger temperature drop through the heating surface of the effect, and hence a higher evaporative capacity.

When evaporation is carried on to high concentrations this factor becomes important. Since the amount of water evaporated in each effect is often nearly the same, the concentration and hence the value of the b.p.r. is not large until the last effects are reached. (See Counter-flow, page 421.)

Removal of Air.—The air or other non-condensable gases may be withdrawn from the system in either of two ways,—first, the condensed steam chest of each effect may be connected direct to the condenser, or second, the steam chest of each effect may be connected to the vapor space of the same effect. Since the presence of non-condensable gas in the steam chest of succeeding effects cuts down the rate of heat transmission (pp. 154 to 157), this second method is advisable only when the percentage of such gas is very small. If the volume of non-condensable gas be large, it is advisable to withdraw it while under the relatively high pressure of each condensed steam chest rather than expend the necessarily increased power incident to withdrawing it by the vacuum pump in the rarefied condition which exists in the condenser.

Heat Recovery from Condensate.—The water leaving the condensed steam chest in a single effect evaporator, or in the first effect of a multiple system, is generally returned to the boiler and its heat content thus utilized. The condensed steam from the other effects of a multiple system is frequently contaminated through entrainment and requires special installation for the recovery of the heat contained therein. Because of the excellent coefficient of heat transfer from condensing steam to boiling liquid, it is more economical to lead the hot condensate from the chest of one effect into the heating coil of the next effect in series. Here, because of the lower pressure, some of this water flashes into steam at the same temperature as the condensing steam in this coil. The temperature of the condensed water in the last effect is too low to make recovery easy and it is therefore discharged through the wet air pump or through the down-take pipe of a barometric condenser.

Starting Up.—To place a multiple effect evaporator in operation quickly and without loss of liquor from boiling over calls for careful and accurate manipulation. Liquor levels must at first be kept very low, and after the vacuum pump is started, water is admitted to the condenser. The first effect should be filled, followed by admission of steam to the steam chest. Feed liquor should be passed on to the following bodies only after it has been heated to the working temperature obtaining there. As soon as the liquor in the last effect has reached the desired concentration, it is allowed to discharge as rapidly as possible without

fall in concentration, and the system now proceeds in smooth and continuous operation.

Such a system will soon adjust itself to a definite temperature and pressure in each effect. The vapor evolved in the first must condense in the coils of the second, where, in turn, it causes the evaporation of a corresponding amount of liquid. If this condensation in the coils of the second does not take place, the steam accumulates, and, backing up, raises the pressure in the first effect, stopping evaporation there. On the other hand, condensation in the coils of the second effect cannot occur without the dissipation of the corresponding heat, and there is no means of absorbing this heat except by evaporating from the boiling liquid in the second effect an approximately equal amount of steam. This interrelation holds for all effects throughout the system, and interference with, or acceleration of, evaporation at any point has its inevitable reaction upon the conditions at every other point. The heat flowing past each section of the apparatus equals that passing every other section, a condition maintained by self-adjustment of the temperature drops through the various heating surfaces and entirely automatic on the part of the system itself.

Probably, the first sign of trouble which the operator observes will be a reduction in evaporative capacity, *i.e.*, it will be found necessary to reduce the rate of discharge of concentrated liquor from the last effect in order to maintain its strength. This undesirable result, however, develops only as a consequence of far-reaching changes in the operating conditions throughout the whole system. This will be made clearer by consideration of the results following specific modification of the operating conditions in a multiple effect system.

Effect of Inadequate Condenser Capacity.—Assume, for example, that, in a system operating normally under given terminal conditions, the temperature of the condenser water rises. The resulting higher temperature of condensation produces immediately a rise in pressure in the last effect, followed by rise in temperature of the boiling liquid. This cuts down the temperature drop through the heating surface in that effect, thus reducing the heat transferred and the steam condensed in the coils. This causes rise of pressure in these coils, backing up the pressure in the effect before the last, and so on back through the whole

system, resulting ultimately in reducing the temperature drop through the heating surface in each effect; hence the evaporation in each is reduced proportionally, with a corresponding decrease in the evaporative capacity of the entire system.

Effect of Increase in Air Leakage, etc.—Again, assume that the operator finds the evaporative capacity of his equipment reduced, but that, in this instance, the cause is either an air leak into the steam chest of an effect in the middle of the system, or the fouling or cutting out of part of the heating surface of the same effect. In either case, in that particular effect both the coefficient of heat transfer and the heat current decrease. Since no effect can continue to receive a heat current greater than it can dissipate, the heat current decreases in *all* effects. As a result the temperature increases in the effect in question, and decreases in all others. Hence the temperature of boiling rises in the preceding effects and falls in the succeeding ones. This redistribution of the magnitudes of the temperature drop through the heating surfaces of the various effects, developing a *high* temperature difference in the body in which the coefficient of heat transfer is decreased, and abnormally *low* values in the others, enables the operator to determine the cause and location of the trouble. An air leak may be distinguished from deficient or defective heating surface by the discrepancy between temperature and pressure in the steam chest. A marked air leak beneath the surface of the boiling liquid will develop the above phenomenon in the next succeeding effect, and in addition cause the temperature corrected for b.p.r. of the boiling liquid [1] into which it was escaping to be lower than would correspond to the pressure above it.

Effect of Steam Leakage.—Three sources of steam leakage are encountered. The first is from the steam chest of an effect into the boiling liquid in that effect, usually through packing at the ends of tubes or through pin-holes caused by corrosion. The second is caused by the bleeding of an excessive amount of steam out of the chest to remove permanent gases. The third is a direct flow of steam from the chest of one effect to that of the next due to imperfect traps in the condensed steam line. The leakage of steam in any of these ways from the chest of an effect results in a relatively low evaporation in that effect.

Modification in operating conditions at any point thus reacts upon and changes the conditions at every other point; but

[1] The thermometer should be immersed in the boiling liquid.

fortunately, as indicated above, analysis of the changes enables the operator to locate and remedy the trouble.

Counter-flow of Liquor and Steam.—Occasionally one encounters solutions in the evaporation of which it is desirable to modify the above outline of multiple operation. Since the viscosity of a solution is greatest when cold and concentrated, the coefficient of heat transfer is lowest [1] in the last effect of a multiple system operated with parallel flow of liquor and steam. Where the product is very concentrated, the coefficient in the last effect may be only 10 per cent, or even less, of that in the first effect. Obviously, then, a higher coefficient will be obtained by evaporating the most concentrated solution at the highest temperature, *i.e.*, in the first, rather than the last effect. In such cases, it may prove worth while to admit the dilute feed liquor into the second effect in the series, allow it to flow thence through to the last, and from there pump it to the first effect for the final concentration. The necessity for such changes is, however, not very frequent.

Choice of Terminal Conditions.—It will be recalled that the evaporative capacity of a multiple system is determined by the amount of heat which can be supplied to the boiling liquid and that this in turn is approximately proportional [2] to the temperature difference between the steam supply and the boiling liquid. The lowest temperature at which the liquid can boil depends on the vacuum in the condenser which in turn is limited by the temperature of the cooling water. The highest allowable temperature is fixed by that pressure of steam supply which the mechanical strength of the apparatus will stand, or by the possible injurious effect which heat may have upon the material to be evaporated. However, the advantages which accrue to high-pressure steam through decrease in the area of the heating surface should be balanced against the resultant decrease in steam economy (p. 438).

Determination of Number of Effects. (*Economic Balance*).—The choice of the number of effects to be used in series in an evaporation system becomes an economic balance of cost of heat

[1] See p. 394.

[2] Since the coefficient of heat transfer increases with the temperature and the temperature difference (p. 394), an effect where a 25° difference is maintained will have more than two and one-half times the evaporative capacity where a 10° F. drop is used.

against fixed charges. If a single effect will handle a certain amount of evaporation, the addition in series of more effects duplicating the first does not greatly modify the evaporative capacity but does cut down the fuel cost. Although the size of the condenser can be reduced, the cost of the auxiliary equipment is not greatly changed; the air pump can be made smaller but not in proportion, because of the greater ratio of dead gas to steam. Liquor pumps remain unchanged. The cost of the effects themselves increases in direct proportion to their number. Therefore, the increase in total cost, and hence in fixed charges, is a little less than proportional to the number of effects. A point is soon reached beyond which the addition of further effects will increase fixed charges and maintenance to more than balance the decrease in cost of heat. This point varies with changing ratios of cost of capital, repairs, and the like, to fuel; under American conditions more than five effects in series are seldom justified; triple and quadruple effects are more frequently met.

As an example of how the most economical number of effects may be calculated, consider the following problem:

Illustration 1.—It is desired to concentrate 400,000 lbs. per day of liquor containing 10 per cent caustic soda to a 35 per cent solution. A suitable type of single effect "salting-out" evaporator of sufficient capacity costs $6400 exclusive of pumps, condenser,[1] and other accessories common to any number of effects. With fixed charges, amortization and interest amounting to 45 per cent per year, the steam at $.40 per thousand lbs. what number of effects should be used to secure maximum economy? Assume $.85n$ lb. of water evaporated per pound of steam, where n=number of effects; 300 operating days per year, and labor the same for any number of effects.

Solution. *Basis*—One operating day.

$$\text{Steam Cost} = 40{,}000 \times \left[\frac{9}{1} - \frac{65}{35}\right] \times \frac{1}{(0.85n)} \times \frac{(0.40)}{(1{,}000)} = \frac{\$134.40}{n}$$

(Lbs. of Solids; Lbs. of Evaporation; Lbs. of Steam)

[1] The condenser must be larger for one effect than for three, as in the latter case about two-thirds of the water evaporated is condensed in the heating surface of the last two effects. In order to simplify this illustration, the variation in the cost of condenser has been neglected as well as the variation in the amount of cooling water.

$$\text{Fixed charges} = \frac{(0.45)\ (6{,}400)\ (n)}{(300)} = \$9.60\,n$$

	One Effect	Two Effects	Three Effects	Four Effects	Five Effects
Fixed charges	\$ 9.60	\$19.20	\$28.80	\$38.40	\$48.00
Steam	134.40	67.20	44.80	33.60	26.88
Total	\$144.00	\$86.40	\$73.60	\$72.00	\$74.88

While these calculations show that the total cost is a minimum for four effects, the total cost for three is so little more that in order to reduce the investment three would be installed. Note that the saving when using three effects instead of one is over seventy dollars per day. While the optimum number of effects varies with the ratio of the cost of steam to the charges on the apparatus, it varies only as the square root of this ratio.[1]

Where fluctuation in the rate of evaporation demanded is likely to arise, it is good engineering to install a multiple effect system with a capacity sufficient for approximately the average load, but with the effects so connected that they can readily be thrown into parallel for the peak load. In this way the normal load is carried with good steam economy, and yet the maximum demand for evaporative capacity is met without the installation of additional equipment, with the consequent fixed charges. It is true that the peak load is carried with poor steam economy but if this load occurs only occasionally, the sacrifice is justifiable. This parallels the practice of the power engineer who designs his steam engine for the normal load, and carries the peak as an overload, though at a poor fuel economy. The auxiliary equipment, pumps, condensers, and the like, must be adequate for the maximum demand. If the increase beyond the capacity of the multiple system be not too great, the effects may be used partly in series and partly in parallel, with less of a decrease in steam economy. By providing for such connections and manipulation,

[1] Since the equation of the total cost curve for this case is

$$\text{Total daily cost} = 9.6n + \frac{134.2}{n}$$

the minimum point will occur where the tangent of the curve has a slope of zero. Hence, one may differentiate the total cost with respect to the number of effects and equate to zero, giving

$$n = \sqrt{\frac{\text{Cost of steam}}{\text{Charges on app.}}} = \sqrt{\frac{134.2}{9.6}} = 3.75$$

considerable flexibility in the operating control of the capacity and heat economy of an evaporative system is possible.

Evaporators are generally operated with the exhaust steam from non-condensing engines. In plants having only small power equipment this arrangement is undoubtedly good, since cheap, yet efficient, reciprocating units are the best to be had. In large power plants, however, especially where turbines are available for the low-pressure stages of the expansion, the steam can be used to as good advantage in the turbine as in a multiple effect system, while the independence resulting from entire separation of the power and evaporator units insures better control of each. If the construction of the evaporator bodies or the character of the liquor is such that full pressure boiler steam cannot be used in the effects, then it is imperative that the steam be expanded down to the safe working pressure for the first effect by passing through a suitable engine, so as to recover the corresponding power which would otherwise be wasted. The best plan, when possible, is to keep the power and evaporator houses entirely separate.

CALCULATIONS FOR EVAPORATOR DESIGN

General Assumptions.—Two important physical properties of a solution affecting evaporator design are, first, the boiling point of the solution as compared with that of the pure solvent, and second, the heat of evaporation of the solvent from the solution. In the design of continuous evaporators for the concentration of relatively dilute solutions (up to perhaps 20 per cent), or for the concentration of stronger solutions under conditions such that the total pressure variations are small (not over 2 or 3 fold), the three following assumptions may be made: first, the b.p.r. of a solution of definite concentration is independent of its temperature and pressure; second, that the heat consumed in the evaporation of a unit weight of solvent from the solution is the same as the heat of evaporation of the pure solvent when volatilized at the temperature of the boiling solution; and third, that the heat capacity of a solution is equal to that of the solvent in it (see Thomsen's[1] Tables. Thus the specific heat of a 10 per cent solution would be 0.9.

[1] J. Thomsen, "Thermochemistry," pp. 161 to 161: Longmans, Green & Co., London (1908).

B.P.R. Due to Solute.—Raoult's law states that the vapor pressure of a solution divided by the vapor pressure of the pure solvent at the same temperature is equal to the mol fraction of the solvent in the solution. Because the molal composition of a solution does not change with the temperature, a corollary of this statement is that the vapor pressure of a solution divided by that of the solvent at the same temperature (normally spoken of as relative vapor pressure, r.v.p.) is the same at all temperatures. The major premise of Raoult's law, that the r.v.p. is equal to the mol fraction of the solvent, holds only in dilute solutions; furthermore, for electrolytes it must be corrected for the degree of dissociation of the solute. Its use in connection with the normal problems of evaporator design is therefore inadmissible. On the other hand, the corollary that the r.v.p. of a given solution is independent of the temperature, holds for relatively strong solutions (perhaps up to 20 per cent) and is a valuable aid in calculation. As dissociation changes but slightly with the temperature, the r.v.p. is practically unaffected by dissociation of the solute.

The assumption that the b.p.r. of a solution is independent of the pressure and temperature is only an approximation, even when that solution follows Raoult's law.

Assume, for example, a solution boiling at 180° C. under a pressure of 4651 mm. Since water at this pressure boils at 160° C., the b.p.r. is 20° C. At 180° C. the vapor pressure of water is 7546 mm., and hence the relative vapor pressure of the solution at 180° C. is $4651/7546 = 0.616$. According to Raoult's law this value should remain unchanged at other temperatures. Assume that the pressure on the solution be reduced so that it boils at 70° C., where the vapor pressure of water is 233.8 mm., the vapor pressure of this solution is, therefore, 0.616×233.8, or 144.1. This corresponds, however, to a temperature of 59.3° C., *i.e.*, the b.p.r. is only 10.7° C. as compared with 20° C. at the higher temperature. In other words, solutions having a constant value of r.v.p. have b.p.r. larger at high temperatures than at low. For example, at 100° C. the above solution has a b.p.r. of 14.1° C.

For concentrated solutions and for calculations involving wide variations in temperature and pressure, the vapor pressure of the solution as a function of concentration and temperature must be definitely known. In the case of the more important solutions it is usually possible to secure the necessary data from the literature. In the absence of such definite information experimental determination must be made.

B.P.R. Due to Hydrostatic Head.—When the heating surface in an evaporator is below the surface of the liquid, the liquid in contact therewith has a higher boiling point than at the surface of the liquid. This can be readily calculated for any particular head. While not strictly accurate, it is a satisfactory approximation to assume for purposes of calculating heat transfer, the average temperature of the boiling liquid to be that at the point midway between top and bottom of the boiling mass.

Disadvantage of B.P.R.—As previously indicated, the total evaporative capacity of a multiple system is directly proportional to total *available* temperature difference, namely, the difference between the temperatures of the steam condensing in the coils of the first effect and the boiling temperature in the last effect, *minus* the total b.p.r. in all effects. Since, for a given capacity, the total heating surface required is an inverse function of the *available* temperature drop, the disadvantage of b.p.r. is obvious.

Estimation of Vapor Pressure. (*Dühring's Rule*).—Since the properties of a solution are a function of two independent variables—*concentration* and *temperature*—the estimation of vapor pressures would be difficult and tedious in the absence of simplifying relationships. Such fortunately exist. The vapor pressure of all materials rises rapidly with the temperature whether the material be a pure solid or liquid substance, a solution of definite constant concentration or a mixture of volatile components. The curvature is very high and a large number of points must be determined to make it possible to draw a satisfactory curve through them. On the other hand, these curves are all similar in shape and this similarity is the basis of the following relationship, stated by *Dühring*[1] in 1878. It is an experimentally determined fact that, if in plotting a vapor pressure curve of any material, instead of plotting the pressures as ordinates against the temperature as abscissas, one plots as ordinates the temperature at which some suitable standard liquid, such as water, exerts the same pressure, the experimental points fall very nearly upon a straight line. The standard liquid chosen should, if possible, be chemically similar to the liquid the vapor-pressure curve of which is being studied. For example, organic hydroxide compounds are best plotted against water, iodine should be plotted

[1] "Neue Grundgesetze zur Nationelle Physik und Chemie," Erste Folge, Leipzig, 1878.

against mercury, since both are monatomic in the vapor state. Hydrocarbons should be plotted against some standard hydrocarbon, etc. It is necessary that the vapor pressure curve of the standard substance chosen be accurately known over a pressure range fully covering the limits desired. It is important, as will develop later, that the heat of vaporization of the standard liquid should be known as a function of temperature. For convenience it is desirable that interpolation tables which give the pressure for small temperature intervals be available. For most purposes, water is a satisfactory standard.

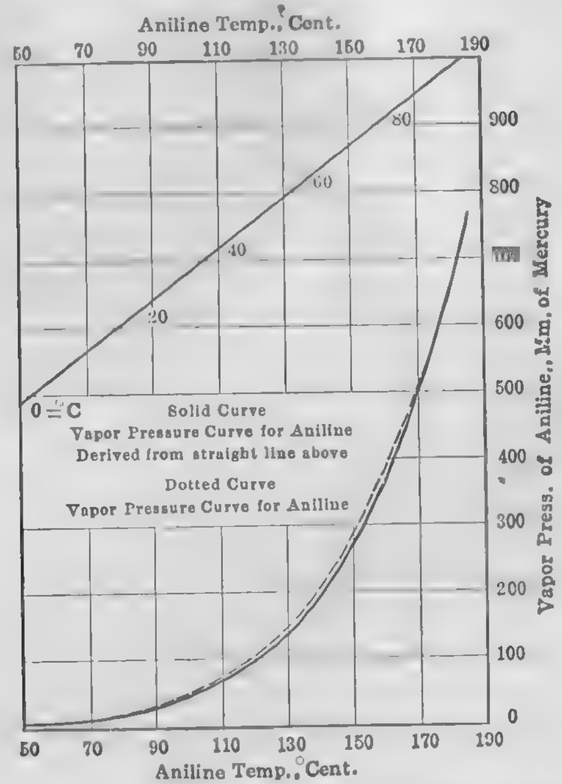

Aniline Temp., °Cent.
50 70 90 110 130 150 170 190
20 40 60 80
0 = °C
Solid Curve
Vapor Pressure Curve for Aniline
Derived from straight line above
Dotted Curve
Vapor Pressure Curve for Aniline
900 800 600 500 400 300 200 100 0
Vapor Press. of Aniline, Mm. of Mercury
50 70 90 110 130 150 170 190
Aniline Temp., °Cent.

FIG. 98.—Dühring's Rule Applied to Vapor-Pressures of Aniline.

It will be clear from the preceding that, since the vapor pressure of a substance plotted in this way gives a straight line, two points in the vapor-pressure curve are theoretically sufficient to determine the line. While it is desirable to have more points, in order to guarantee accuracy, a large number is not essential. This means that from a small number of determinations of the

vapor pressure of any material of constant composition, the vapor-pressure curve of that material can be constructed with satisfactory accuracy.

To show the applicability of this method, a vapor-pressure curve for aniline is given in Fig. 98. The straight line represents temperatures of aniline (abscissas) plotted against temperatures at which water has the same vapor pressure. The solid curve is the vapor-pressure plot derived from the straight line. The dotted curve shows experimental values.[1] This indicates the accuracy of the method.

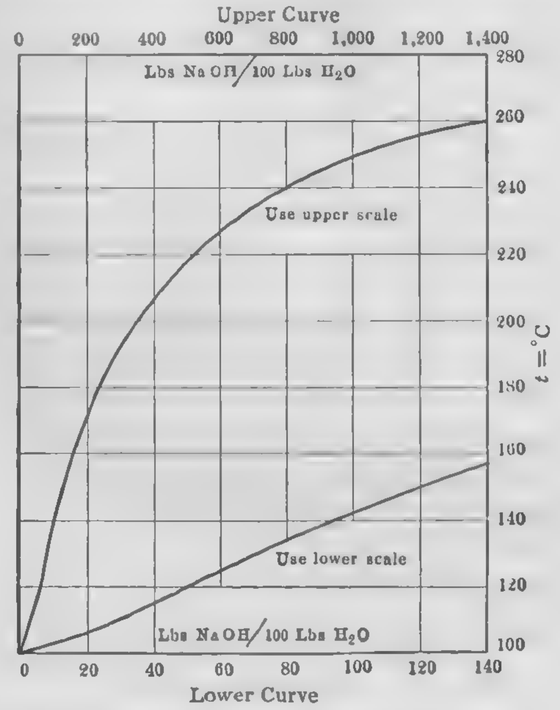


FIG. 99.—Boiling Points of Caustic Solutions.

If it is possible to find in the literature the vapor-pressures of a given solution at two different temperatures, it is theoretically possible to construct its vapor-pressure curve for any temperature range. Further data serve as checks. For example, the vapor-pressure curve of caustic soda solutions has been determined at 0° C., by Dietterici,[1] at 100 C., by Tamman,[2] and the boiling points of these solutions are also known (Fig. 99).

[1] "Landolt-Börnstein Tables." [2] *Ibid.*

This gives, therefore, three points on the vapor-pressure curve of any caustic solution. From these data Fig. 100 has been constructed. On this plot the pressure itself has not been indicated because over the extremely wide temperature range employed, the variation in pressure is excessive and would not be satisfactorily represented diagrammatically. According to Dühring's rule each of these curves should be a straight line. Note that the curves lie quite close together below 25 per cent but at high concentrations the vapor pressure differences are very great. Further illustrations of the use of Dühring's rule are given in recent literature.[1]

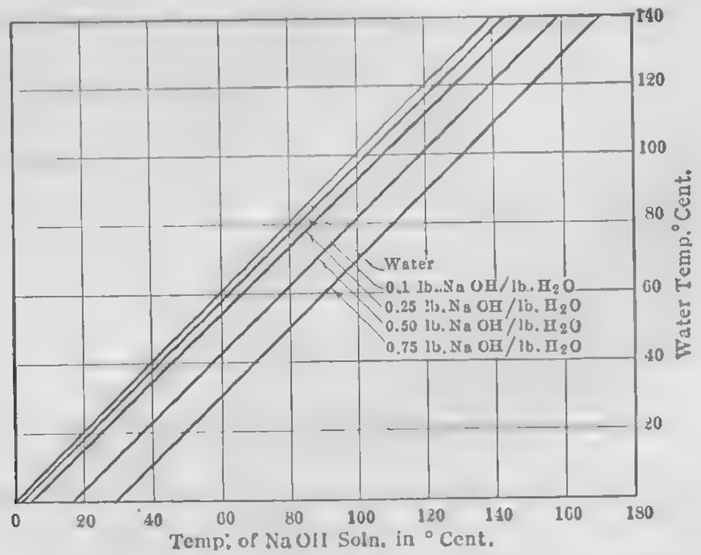


FIG. 100.—Dühring's Rule Applied to Vapor-Pressures of Caustic Solutions.

Estimation of Heat of Vaporization.—The second most important datum which it is necessary to have with regard to a liquid is its heat of vaporization. This is connected with the vapor pressure curve by the Clausius equation.

From these "temperature versus temperature plots" derived from vapor-pressure data, it is also possible to secure an accurate estimate of the heat of vaporization, as follows:

Write the Clausius equation (in its approximate form) both

[1] E. M. BAKER and V. H. WAITE, *Chem. Met. Eng.*, vol. 25, No. 25 (Dec. 21, 1921), and B. F. DODGE, *J. Ind. Eng. Chem.*, vol. 14, No. 6, p. 569 (June, 1922).

for the liquid or solution in question and for the standard liquid with which it is being compared, *i.e.*,

$$\frac{dp}{pdT}=\frac{Q}{RT^2} \quad \text{and} \quad \frac{dp_w}{p_w dT_w}=\frac{Q_w}{RT_w^2},$$

wherein p; T; Q = vapor pressure; absolute temperature; molal heat of vaporization; of the liquid or solution in question;
p_w; T_w; Q_w = vapor pressure; absolute temperature; molal heat of vaporization; of the *standard* liquid used for comparison.

Dühring has shown that if p_w be taken to equal p, T_w becomes a straight line function of T. Since, if $p_w=p$, $dp_w=dp$, there results the relationship

$$Q=Q_w\frac{T^2}{T_w^2}\frac{dT_w}{dT},$$

i.e., from the slope (dT_w/dT) of the "temperature versus temperature" plot described above, and the known value of the heat of vaporization of the standard liquid, one can calculate the unknown heat of vaporization of the liquid under consideration.

For example, the heat of vaporization of aniline at 100° C. is found as follows. As shown by Fig. 98, the temperature (t_w) at which the standard liquid (water) has the same pressure as aniline at 100° C. is 36° C., so

$$T_w=273+36=309, \quad \text{and} \quad T=373.$$

Fig. 98, p. 430, shows that $dT_w/dT=0.757$. From the steam tables, the heat of vaporization of water at 36° C.=1,038 B.t.u. per lb., so $Q_s=(18)\ (1{,}038)$. Then

$$Q=\frac{(18)\ (1{,}038)\ (373)^2\ (0.757)}{(309)^2}=20{,}500 \text{ B.t.u. per lb. mol of aniline,}$$

or 20,500/93=221 B.t.u./lb. aniline.

The solution of a few practical problems will illustrate these principles.

Illustration 2.—Assume a single vacuum pan of the submerged tube type, operating continuously and provided with a condenser capable of giving a vacuum of 26 in. of mercury (Bar. 29.91 in.). The heating coils have an overall coefficient (H) of heat flow of 100 B.t.u. per hr. per ° F. per sq. ft., and use exhaust steam at 6 in. vacuum. What is the heating surface required per 100 lbs. of entering liquor per hour to concentrate 2 per cent NaOH, entering at 65° F., to a 25 per cent solution?

Solution.—It is first necessary to calculate the terminal temperatures of the system. The temperature in the steam chest will correspond to the 6-in. vacuum maintained (200.8° F.). Since the liquor must leave the effect at a concentration of 25 per cent the boiling liquor within the effect must be at this concentration. The temperature within the effect will equal that corresponding to a 26-in. vacuum (124.2° F.) plus the b.p.r. of a solution of 33⅓ parts NaOH in 100 parts water. This latter [1] is 11.5° C., or 20.7° F. as determined from Fig. 100, page 427. By the assumption that the b.p.r. is the same at all temperatures, one finds that the temperature maintained within the effect is 124.2° F.+20.7° = 144.9° F. By assumption that the heat necessary to vaporize water from a solution equals the heat of vaporization of the water alone, at the boiling temperature of the solution, one finds from the steam tables that 1010 B.t.u. is the heat of vaporization at 144.9° F. In each 100 lbs. of liquor entering there are 98 lbs. of water and two pounds of NaOH. As the amount of NaOH is unchanged in passing through the system, it is taken as the basis of calculation; 6 lbs. of water leave with each 2 lbs. NaOH (25 per cent solution) or 92 lbs. of water are evaporated per 100 lbs. of entering liquor, so the heat to vaporize the water equals 92×1010 B.t.u. By the assumption that the specific heat of a solution equals that of the water alone, to heat 100 lbs. entering 2 per cent liquor 100 (144.9−65) (0.98) B.t.u. are necessary. The area of heating coils (A) can now be determined by the use of Newton's law (p. 386):

$$\frac{Q}{\theta} = [100\ (144.9-65)\ (0.98)+92\ (1010)] = 100A\ (200.8-144.9).$$

Whence, $A = 18.0$ sq. ft. per 100 lbs. of feed liquor per hour.

Illustration 3.—In the previous problem, what would be the heating surface required, if the depth of the boiling liquid in the effect be four feet? (Sp. Gr. = 1.3).

Solution.—The absolute pressure above the boiling liquid is

$$(29.91-26)\ (14.7)/(29.9) = 1.92 \text{ lbs. per sq. in., and}$$

the average pressure due to the hydrostatic head = (2) (1.3) (62.4)/(144) = 1.13 lbs. per sq. in., so the average total pressure = 1.92+1.13 = 3.05 lbs. per sq. in., which corresponds to a temperature of 142.6° F. To this must be added the b.p.r. of 20.7, giving the operating temperature of 163.3° F. As the steam leaves the surface of the liquid, where the pressure corresponding to the vacuum is maintained, the heat of vaporization will be the same as in the previous problem, or

$$\frac{Q}{\theta} = [(100)\ (163.3-65)\ (0.98)+92\ (1010)] = 100A\ (200.8-163.3),$$

whence, $A = 27.3$ sq. ft., an increase of over 50 per cent.

[1] B.p.r. due to hydrostatic head is neglected here, but see problem following.

EQUATIONS FOR MULTIPLE EFFECT EVAPORATION (CONTINUOUS AND PARALLEL FLOW OF STEAM AND LIQUOR)

The following symbols will be used in the formulation of heat balances for multiple effect evaporation:

c = Parts solute per part solvent by weight;
W = Weight of solvent in the liquor per unit of time;
t = Temperature of solution;
T = Temperature of steam in heating coils;
r = Heat of evaporation of unit weight of solvent from either solution, or pure solvent;
s = Specific heat of solution;
A = Area of heating surface in an effect;
H = Overall coefficient of heat transfer through the heating surface, *i.e.*, from condensing steam to boiling liquor;
Q = Amount of heat transferred *through heating surface* per unit of time.

Subscripts.—(0) for material entering the first effect,
(1) applies to the first effect, or material leaving it,
(2) applies to the second effect, or material leaving it, etc.
(a) before the symbol indicates that it applies to the condition within the heating coil,
(b) refers to the boiling solution.

Thus W_0 is the weight of solvent entering the first effect per unit time, and c_0 is its concentration. The temperature of the steam in the coils of the second effect is T_2, while the boiling solution is at t_2. The heat of condensation of this steam in the coils is $({}_ar_2)$ while the heat of vaporization of the solution is $({}_br_2)$.

If the solute be non-volatile, the amount entering and leaving each effect of the series per unit time will be constant. Otherwise, there would be an accumulation of the solute in some one effect. This is expressed mathematically by:

$$c_0W_0 = c_1W_1 = c_2W_2, \text{ etc.}$$

The solvent evaporated in the first effect is $W_0 - W_1$, in the second, $W_1 - W_2$, etc. The heat transmitted through the heating surface in the first effect must preheat the feed to the boiling temperature and evaporate the solvent.

$$Q_1 = W_0(1+c_0)\ [1]\ s_0(t_1-t_0)+(W_0-W_1)\ ({}_br_1) = H_1A_1\ (T_1-t_1).$$

[1] As pointed out on p. 427, in many cases the product $(1+c)s$ is practically equal to unity.

For the sake of illustration, assume that the condensed steam is removed from the system from each steam chest. The steam rising from the first effect is superheated, and cools on entering the second effect, giving up its superheat, and then condenses, giving up its heat of vaporization. Where the superheat, namely the b.p.r., is small (10° F. or less) this superheat can be neglected without vitiating the calculations, *provided* one remembers that $T_2=t_1$ less the b.p.r. in the first effect. The heat transmitted through the heating surface of the second effect is:

$$Q_2=(W_0-W_1)\,[(0.48)\,(t_1-T_2)+({}_ar_2)]=H_2A_2\,(T_2-t_2).$$

The evaporation in the second effect is greater than corresponds to this heat supply through the heating surface, as the liquor entering from the first effect is superheated with respect to the pressure in the second effect, because it is at the boiling point corresponding to a higher pressure, namely, that in the first effect, and hence gives up a corresponding amount of heat, available for evaporation in this second effect. This is the so-called *self-evaporation* of a multiple effect system, and is expressed by the second term in the following equation:

$$Q_2+W_1\,(1+c_1)\,(s_1)\,(t_1-t_2)=(W_1-W_2)\,({}_br_2).$$

ILLUSTRATIVE PROBLEMS IN MULTIPLE EFFECT EVAPORATION

Instead of using the above equations, one may develop the desired equations during the solution of the problem, using as tools the equality of input and output of matter and of heat, and Newton's law applied to the transfer of heat through the heating surface.

The following problem shows that where high-pressure steam and *cold* feed liquor are used in multiple effect practice, the evaporation per pound of steam is considerably less than the number of effects.

Illustration 4.—In a certain four-effect evaporator provided with equal heating surface in each effect, 56.5 lbs. of water are evaporated from each 100 lbs. of feed liquor, the b.p.r. being negligible even at the highest concentration. Feed liquor enters at 100° F., the available steam pressure is 52 lbs. gauge, the jet condenser water is at 100° F., giving a vacuum in the last effect of approximately 3.5 in. of the barometer, which corresponds to a boiling

temperature in the last effect of 120° F. Assume that the condensed steam from each steam chest is withdrawn immediately from the system.

1. (*a*) Per 100 lbs. of entering liquor, calculate the pounds of water evaporated in each of the four effects.

(*b*) What percentage of the total heat entering the first effect produces evaporation in that effect?

(*c*) Tabulate the ° F. temperature drop in each effect.

(*d*) Calculate the lbs. of water evaporated per lb. of steam fed to the first effect. Explain why this figure is much less than 4 in this case.

NOTE.—In order to simplify the calculations, assume the heat of vaporization of water and heat of condensation of steam as 1000 B.t.u. per lb.; take specific heat of liquor as unity; and assume no heat losses to the surroundings. Overall coefficients of heat transfer from steam to liquor are 400, 350, 300 and 200 B.t.u. per hr. per ° F. per sq. ft. of heating surface in the first, second, third and fourth effects, respectively.

Basis: 100 lbs. of entering liquor.

Let the lbs. of steam arising from the first effect be x_1, that from the second x_2, etc., and the lbs. of steam fed to the first effect be S.

(*a*) Equating the B.t.u. input and output of each effect beginning with the first, gives the four equations following, on the basis of 100 lbs. of entering liquor:

$$1{,}000S=100(t_1-100)+1{,}000x_1, \quad (1)$$
$$1{,}000x_1+(100-x_1)(t_1-t_2)=1{,}000x_2, \quad (2)$$
$$1{,}000x_2+(100-x_1-x_2)(t_2-t_3)=1{,}000x_3, \quad (3)$$
$$1{,}000x_3+(100-x_1-x_2-x_3)(t_3-120)=1{,}000x_4. \quad (4)$$

Calling Q the B.t.u. transferred through the heating surface per 100 lbs. of entering liquor, and y the hundred-weights of feed liquor per hour,

$$A=\frac{Qy}{(H)\,(T-t)}.$$

Since $Q_1=1{,}000S$, $Q_2=1{,}000x_1$, $Q_3=1{,}000x_2$, and $Q_4=1{,}000x_3$, $A_1=A_2=A_3=A_4$, and $T_2=t_1$, $T_3=t_2$, $T_4=t_3$, one may write Newton's law as follows:

$$A_1=\frac{1{,}000Sy}{(400)\,(300-t_1)}=A_2=\frac{1{,}000x_1y}{(350)\,(t_1-t_2)}, \quad (5)$$

$$A_2\ \frac{100x_1y}{(350)\,(t_1-t_2)}\ =A_3=\frac{1{,}000x_2y}{(300)\,(t_2-t_3)}, \quad (6)$$

$$A_3\ \frac{1{,}000x_2y}{(300)\,(t_2\quad t_3)}\ =A_4=\frac{1{,}000x_3y}{(200)\,(t_3\quad 120)}. \quad (7)$$

$$\text{Also, } x_1+x_2+x_3+x_4=56.5. \quad (8)$$

Solving by "trial and error,"[1] the following values are found to approximately satisfy the above eight equations:

$x_1 = 10$ lbs.	$S = 24.63$ lbs.
$x_2 = 12.3$ lbs.	$t_1 = 246.3°$ F. $= T_2$.
$x_3 = 15.1$ lbs.	$t_2 = 221.3°$ F. $= T_3$.
$x_4 = 19.1$ lbs.	$t_3 = 185.5°$ F. $= T_4$.

(*b*) Heat used for vaporization in first effect = 10,000 B.t.u. Heat used for warming entering liquor = 14,630 B.t.u.

Per cent heat furnished used for vaporization in first effect,

$$\frac{10{,}000}{24{,}630} = 40.7 \text{ per cent.}$$

(*c*) Temperature difference in effects 1, 2, 3, and 4.

$$T_1 - t_1 = 53.7° \text{ F.}$$
$$T_2 - t_2 = 25° \text{ F.}$$
$$T_3 - t_3 = 35.8° \text{ F.}$$
$$T_4 - t_4 = 65.5° \text{ F.}$$

(*d*) $\dfrac{x_1+x_2+x_3+x_4}{S} = \dfrac{56.5}{24.6} = 2.30$ lbs. evap./lb. steam.

So 10.0 lbs. of steam are used directly for evaporation, the other 14.6 lbs. (59.3 per cent of the total) being stored up in the liquor and used in self-evaporation in the lower effects; this storing up of the heat is a disadvantage, in that the heat stored is not re-used quantitatively as many times as there are effects. In a multiple system of any given number of effects, the greater the proportion of the heat supply stored in the liquor in the first effect, the less will be the total evaporation in all effects per pound of initial steam. In a given system operating under fixed terminal conditions, the percentage of heat obtained from the initial steam stored up in the feed liquor will be high where the ratio of weight of feed liquor to the evaporation in the first effect is high, and where the temperature of the feed is far below the boiling temperature in the first effect. In the example just given, the steam economy calculated is poor (2.30 lbs. of evaporation per lb. of steam). This is primarily due to the large amount of heat stored up in the liquor in the first effect, and to a lesser degree due to the fact that the heat in the condensate from the various steam chests was not utilized. If the condensed steam from each chest, instead of being withdrawn from the system as assumed above, be passed on to the effect below, the lbs. of evaporation per lb. of steam fed will increase somewhat.

[1] One method of accomplishing this is to assume trial values of the evaporation and of the temperature in each effect and test the assumed values by Newton's law, Eqs. (5), (6) and (7), since when suitable values are found, these three equations will check. If the correct values of the latent heat are used in solving this problem, instead of a value of 1000 B.t.u. per lb. throughout, the answers will not change greatly.

EQUATIONS FOR THEORETICAL ENERGY REQUIRED IN EVAPORATION.

To separate a solvent from its solution, if p_0 = pressure of the solvent at the temperature in question, p that of the solution, R the gas constant, and T the absolute temperature, using as the basis of calculation an amount of solution containing one mol of non-volatile solute and N mols of solvent, the free energy required (W) is

$$W = RT\int_{N_2}^{N_1} ln\frac{p_0}{p}dN. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The units in which the work-energy involved are expressed depend on the units in which R is given. This expression is exact, barring deviations from the gas laws, which are usually small at the pressures at which evaporating processes are operated. For any given case the equation may be evaluated by graphical integration, but to show how small is the real energy requirement in evaporation, it is possible to integrate this expression by the assumption of Raoult's law; in the worst case this will give a rough approximation, but in many cases the deviation will be only a few per cent. The result is

$$W = RT\, ln\left[\frac{(N_2)^{N_2}(N_1+1)^{N_1+1}}{(N_1)^{N_1}(N_2+1)^{N_2+1}}\right],$$

where N_1 and N_2 represent the mols of solvent associated with one mol of solute at the beginning and end of the evaporation, respectively.

For the total removal of the solvent from a non-volatile residue with which the solvent is completely miscible, *i.e.*, where no crystallizing of the residue occurs nor separation as a distinct phase, *e.g.*, when $N_2 = 0$, this becomes

$$W = RT\, lnN_1\left[\frac{N_1+1}{N_1}\right]^{N_1+1}$$

In the evaporation of a saturated solution of the solute, during which crystallization or separation occurs,

$$W = N_s RT\, ln\frac{N_s+1}{N_s} = N_s RT\, ln\frac{p_0}{p_s}$$

where N_s = mols solvent per mol of solute in the saturated solution and p_s = pressure of that solution. For the evaporation of a dilute solution to saturation, followed by crystallization, this last equation applies only to the second stage of the process, the work consumption of the first stage being determined by the general equation given above.

To illustrate, assume the complete removal of water from a 10 per cent glycerine solution at 90° F.; *i.e.*, of 9 times 92 or 828 lbs. of water from 1 lb. mol (92 lbs.) of glycerine. $N_1 = 828/18 = 46$, $R = 1.99$.

$$W = 1.99\ (550)\ ln\ 46\left[\frac{47}{46}\right]^{47} = 5290 \text{ B.t.u.}$$

or $5290 \div 828 = 6.4$ B.t.u. per lb. of water evaporated.

It is evident that the more concentrated the solution the greater the energy consumption per pound of water evaporated, but even for strong solutions this quantity remains small. For colloidal solutions, *i.e.*, those of high molecular weight the necessary work is negligible, as is obvious from the fact that the pressure of such solutions is practically the same as that of the pure solvent. For water, the theoretical work of evaporation is zero. As stated, even for true solutions the value is low.

CHAPTER XIV

HUMIDITY, AND WET AND DRY BULB THERMOMETRY

The amount of water vapor present in a gas is spoken of as the "humidity" of that gas. The design of apparatus of great industrial importance for such processes as the drying of solids by gases, the drying of saturated gases by liquids, the cooling of liquids by their evaporation into gases (cooling towers, spray ponds, etc.), depends upon a clear conception of this quantity, and convenient units in which to express it.

The term "relative humidity" [1] is much used in meteorology and means the amount of water vapor which is present in a definite volume of air at any temperature expressed as a percentage of the amount which is present in an equal volume of air when it is completely saturated at the same temperature.[2] This unit is inconvenient for engineering calculations because there is present no constant quantity to serve as a basis for computation. Thus if air be completely saturated by introducing water vapor into it at constant temperature, either the volume of the mixture, or its total pressure, must increase. Furthermore if a mixture of air and water vapor be heated at either constant pressure or constant volume, the relative humidity will decrease rapidly, despite the fact that the composition of the mixture expressed by either weight or volume remains unchanged.

DEFINITIONS

William Grosvenor[3] has proposed a system of units which is admirable for the purpose of this work and with some modifica-

[1] This is also spoken of as percentage relative humidity or percentage humidity. As will appear on page 442, the term percentage humidity is used in a different sense throughout this book.

[2] Relative humidity is defined as $100p/p_s$, where p is the actual partial pressure of the water vapor and p_s is the vapor pressure of water at the same temperature. For example, if a mixture of air and water vapor at 100° F. has a partial pressure of water vapor of 24.35 mm. of mercury, since the vapor pressure of water at this temperature is 48.7 mm., the relative humidity equals 100 (24.35/48.7), or 50 per cent.

[3] *Trans. Am. Inst. Chem. Eng.*, vol. 1, 1908.

tions it will be adopted. The basis of all calculations is one part by weight of dry air. While any unit may be employed, the pound will be used here. The following definitions will be adhered to in this book:

Humidity (H) is the number of pounds of water vapor carried by one pound of dry air.[1]

Percentage Humidity is the number of pounds of water vapor carried by one pound of dry air at a definite temperature, divided by the number of pounds of vapor which one pound of dry air would carry if it were completely saturated at the same temperature. In other words, it is the humidity of air at any temperature expressed as per cent of the humidity of saturated air at the same temperature. *It should be noted that this definition of percentage humidity is not the same as per cent relative humidity, and the two should not be confused.*

Dew Point[2] is the temperature at which a given mixture of air and water vapor is saturated with water vapor. In other words, it is the temperature at which water exerts a vapor pressure equal to the partial pressure of the water in the air.

Humid Heat (s) is the quantity of heat necessary to raise the temperature of one pound of dry air plus such water vapor as it contains, one degree Fahrenheit. Humid heat obviously increases with increasing vapor content of the air, and is therefore a function of humidity.

Since over the range of temperature involved the specific heats of dry air and water vapor are substantially constant, being 0.238[3] and 0.48, respectively, the following equation is used to calculate the humid heat: $s = 0.238 + 0.48\,H$.

Humid Volume is the volume in cubic feet of one pound of dry air together with the water vapor it contains. It is influenced by temperature, pressure[4] and humidity.

Saturated Volume is the volume in cubic feet of one pound of dry air when it is saturated with water vapor; that is, it is the humid volume *at saturation*, and is determined by the temperature and pressure. It should be noted that the humid volume of air equals the product of its saturated volume at its dew point and the ratio of the absolute temperature of the air to the absolute temperature of its dew point.

[1] This is sometimes called absolute humidity.

[2] Called "dew point," because if air be cooled below this temperature liquid water begins to separate.

[3] See p. 454.

[4] In the discussion and calculations following, the total pressure is taken as normal barometric, unless otherwise stated.

Wet Bulb Temperature is the *dynamic* equilibrium temperature attained by a surface wetted with water, when exposed to air under "adiabatic" conditions. Under these conditions the heat flowing from the warmer air to the wetted surface is quantitatively consumed in vaporizing the water, and hence the temperature of the wetted surface is constant.

For unsaturated air the wet bulb temperature will always be between that of the air (the "dry bulb" temperature) and the temperature where condensation would begin (the dew point). For saturated air, all three temperatures become identical. A detailed discussion of wet bulb temperature is given on pp. 444 to 447.

DETERMINATION OF HUMIDITY

Although the water content of air may be determined by chemical methods, in practically all engineering work the humidity is calculated from observations of the "wet" and "dry" bulb temperature of the air. The mechanism of the process will be considered in detail, not only because of its intrinsic importance, but also on account of the light thrown on all the phenomena of evaporation of a liquid into a gas.

Mechanism of Evaporation of a Liquid into a Gas.—If a drop of water at a temperature slightly above the dew point be placed in an inert gas, for example, air of less than 100 per cent humidity, vaporization will take place. Inasmuch as the water vapor is carried away from the drop by diffusion, the rate of evaporation will be proportional to the area of the drop and to the difference between the vapor pressure of the drop and the partial pressure of water vapor in the surrounding air. Calling the surface area of the drop A, its temperature t_1, its vapor pressure p_1, its weight w, the partial pressure of aqueous vapor in the surrounding air p_a, the air being at t_a, the evaporation dw per differential time $d\theta$ is given by

$$\frac{dw}{d\theta} = k.1(p_1 - p_a),$$

where k is the diffusion coefficient through the *gas film* on the drop.

If the temperature of the air is higher than that of the drop, an amount of heat, dQ, will flow from the air to the drop as expressed by Newton's law:

$$\frac{dQ}{d\theta}=hA(t_a-t_1)$$

where h is the coefficient of heat transfer through the *gas film* on the surface of the drop.

This heat transfer from the air will raise the temperature of the drop, thus increasing the evaporation but reducing the rate of heat inflow. This process will continue until ultimately a condition of dynamic equilibrium is reached in which the heat inflow from the surrounding air will exactly supply the heat of vaporization of the water evaporating. Mathematically expressed,

$$\frac{dQ}{d\theta}=r\frac{dw}{d\theta}=kAr(p_1-p_a)=hA(t_a-t_1),$$

where r is the heat of vaporization per unit weight of water. This simplifies to

$$p_1-p_a=\frac{h}{kr}(t_a-t_1),$$

or since the heat of vaporization of water varies but little over quite wide temperature ranges, one may write,

$$p_1-p_a=K(t_a-t_1), \text{ where } K \text{ has replaced } h/kr.$$

Although the above equation for adiabatic evaporation of water into unsaturated air is based on the assumption that the water was initially colder than the air, it is obvious that the same condition of dynamic equilibrium described above will be obtained regardless of the initial water temperature. Thus, if the initial water temperature is higher than that of the air, the water will be cooled, not only by evaporation, but also by heat transfer from the drop to the air by conduction and convection.

Wet and Dry Bulb Thermometers (Hygrometers).—If a drop of liquid be left in a gas, it rapidly assumes the equilibrium condition represented by this equation, and use is made of this fact to determine the water content of the air. The temperature of the air, t_a, is measured with an ordinary mercurial thermometer, while the surface of the bulb of a second thermometer is kept wet by being enclosed in a cloth or wick moistened with water. This "wet bulb" rapidly assumes the equilibrium temperature given by the above equation, which, for this dynamic equilibrium shall be called t_w. (The thinner the wick the more rapidly is this temperature attained, but if the cloth be too thin, the water is likely to disappear too rapidly for the mercury to reach the true equilibrium temperature.) The unknown partial pressure of water vapor in the air is

$$p_a=p_w-K(t_a-t_w)=p_w-\frac{h}{kr_w}(t_a-t_w) \quad . \quad . \quad . \quad . \quad (1)$$

Since t_a and t_w may be observed, and p_w can be read from the steam tables to correspond to the temperature of the wet bulb, t_w, a knowledge of K enables one to determine the amount of water in the air for any condition of temperature and humidity. Allowing for these variations[1] in K, the above equation is the basis of all humidity tables and charts. It is found to be a function of both the total pressure and of the temperature, but the change is sufficiently small to be negligible for many engineering calculations. Thus, if temperatures be given in degrees Centigrade and pressures of water vapor in millimeters, K is practically 0.50 for water in air at normal barometric pressure. The difference of the "dry bulb" and "wet bulb" temperatures is sometimes called the "depression" or "psychrometric difference."

Elimination of Error Due to Radiation.—The diffusion coefficients of both vapor and heat through the gas film vary greatly with the relative velocity of the gas past the liquid surface.[2] However, the influence of velocity on both processes should, theoretically, be due solely to the diminution of the thickness of the gas film on the surface of the liquid. Furthermore, the diffusion of both gas and heat should be inversely proportional to the effective thickness of that film, and hence the ratio of the two diffusion constants, h/k, should remain independent of the velocity, *i.e.*, K should have a definite, constant value, whatever the velocity. Experimentally such is found to be the case

[1] The quantities affecting K will be discussed later.

[2] See pp. 36 to 42.

when the error due to radiation to the wet bulb from the surroundings is eliminated. The heat received by radiation is constant for definite temperature conditions, entirely independent of air velocity; by increasing the air velocity, the heat received by conduction can be increased to such a degree as to render the radiation a quantity negligible in comparison. Since the surroundings are usually at the dry bulb temperature, radiation raises the temperature of the wet bulb, *i.e.*, use of the above equation, in absence of forced air velocity is equivalent to an increase in the value of K. As a matter of fact, the value of K obtained from hygrometers of the stationary type is always too high. As motion of air over the surface is increased, K decreases, asymptotically approaching a constant value. Since it is difficult to keep the air perfectly still, and since when the motion is slight a small change in the velocity produces a large variation in K, it is obvious that the velocity of air must be such as to produce this minimum *constant* value of K. The necessary motion is secured in the standard instrument by mounting the thermometers on a stick with a handle attached (*sling psychrometer*) so that they may be swung by hand until constant readings are obtained. In some cases instead of swinging the thermometers, air is sucked by the thermometers by a fan (to avoid heating effect on the air passing through the fan). For this reason, the humidity of air at a given point in a drier, or other apparatus in which the air velocity is high, may be obtained from the readings of stationary thermometers.

Technique of Psychrometry.- The technique of the use of a sling psychrometer is important. Attention has already been called to the fact that a high *relative* velocity must be maintained between the wet bulb and the air so that any radiation from the surroundings to this wet bulb is negligible compared with the heat picked up by convection and conduction from the air. It was also pointed out that the bulb must be definitely wet at the time the wet bulb reading is taken. For exact work, before the bulb is swung, the temperature of the wetted bulb should be adjusted to a point just above the true wet bulb temperature of the air being tested. If the initial temperature of the water on the bulb is too high it will take a long time to cool the bulb down to the wet bulb point and before this point is reached the water will have evaporated to such an extent that the thermometer never reaches

the true wet bulb temperature. (See Curve 1, Fig. 101.) If the initial temperature of the wet bulb is but slightly above that corresponding to the true wet bulb reading the thermometer will cool quickly to the wet bulb temperature long before the water has evaporated to any serious extent and a long flat minimum in the temperature curve will be observed. (See Curve 2, Fig. 101.) If, however, the initial temperature is below that of the true wet bulb reading the thermometer will rise in temperature throughout the period of slinging. It is true that there will be a flat portion in the temperature curve as shown by Curve 3, Fig. 101, but the estimation of this point of inflection is obviously inaccurate. The observer can be sure of the accuracy of the determination of the wet bulb point only by using water at a temperature only slightly above the true wet bulb temperature and by reading the wet bulb thermometer at different times during the slinging and noting the minimum temperature obtained.

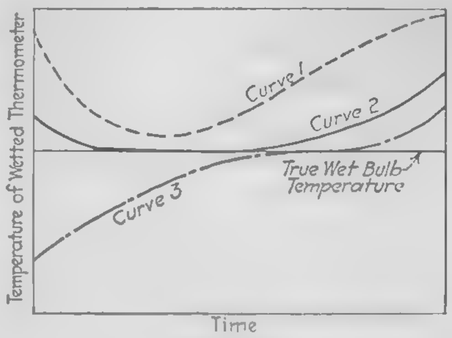


FIG. 101.

CONSTRUCTION OF HUMIDITY CHART

In Fig. 102[1] the following four items are plotted as ordinates *against temperature in ° F. as abscissas*:

1. *Humidity* (H) as pounds of water per pound of dry air.
2. *Specific Volume*, as cu. ft. of dry air per pound of dry air.
3. *Saturated Volume*, as cu. ft. of saturated mixture per pound of dry air.
4. *Latent heat of steam*, r, as B.t.u. per pound of water vaporized.

In addition, there are shown:

5. The *humid heat* (s), plotted as abscissas against the humidity (H) as ordinates, and
6. "*Adiabatic*" Cooling Lines.

[1] This is based on the chart published by The Institute of Chemical Engineers (*loc. cit.*), except that humid heat is plotted against humidity, instead of temperature.

The construction of each of these curves will now be taken up in the order named. *This chart represents mixtures of dry air and water vapor, the total pressure of the mixture being taken as normal barometric.*

1. Humidity, H.—Taking the *actual* pressure of water vapor in the mixture as p millimeters of mercury, the pressure of the

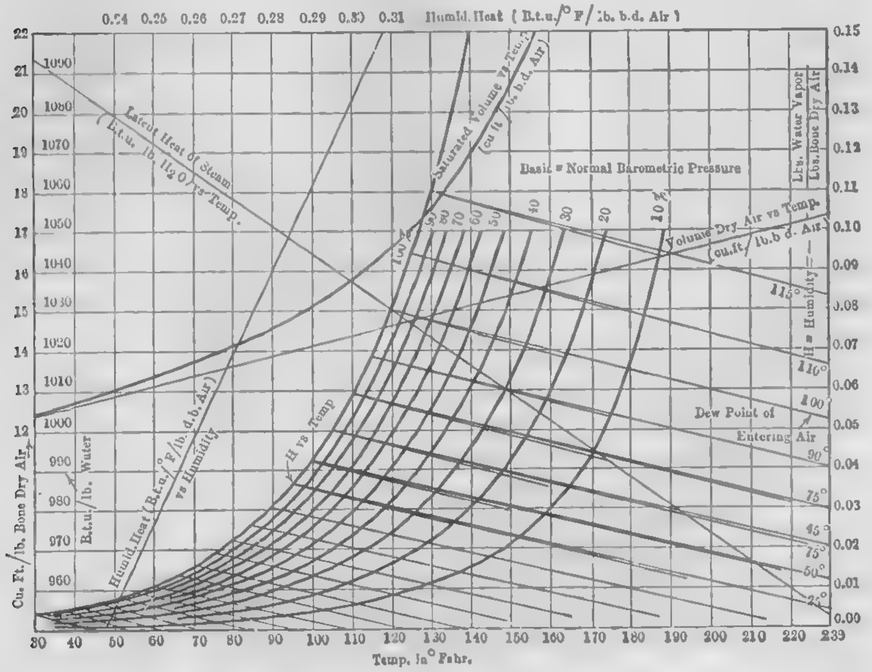

Humid. Heat (B.t.u./° F./lb. b.d. Air)
Latent Heat of Steam (B.t.u. / lb. H2O) vs Temp.
Saturated Volume Vs Temp. (cu. ft. / lb. b.d. Air)
Basis = Normal Barometric Pressure
Lbs. Water Vapor / Lbs. Bone Dry Air
Volume Dry Air vs Temp. (cu. ft. / lb. b.d. Air)
H = Humidity = —
Dew Point of Entering Air
Cu. Ft. / lb. Bone Dry Air
B.t.u. / lb. Water
Humid. Heat (B.t.u. / ° F. / lb. d.b. Air) vs Humidity
H vs Temp
Temp. in ° Fahr.

FIG. 102.—Humidity Chart, Ordinary Range.

(This chart is reproduced to a larger scale on the folding chart facing page 738.)

dry air is obviously equal to $760-p$. Since the molal ratio of water vapor to air is $\frac{p}{760-p}$, the weight ratio is

$$H=\frac{(p)\quad(18.02)}{(760-p)\quad(29)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as pounds of water vapor per pound of dry air.

The curve in Fig. 102 marked "100 per cent" is calculated by substituting in the preceding equation the *saturation* pressure of water vapor at various temperatures, data being taken from the steam tables. For example, the saturation pressure of water

vapor at 100° F. is 48.7 mm. of mercury, and hence H at saturation at 100° F. is

$$\frac{48.7\quad(18.02)}{711.3\quad(29)}=0.0426.$$

The percentage saturation curves are obtained by taking the corresponding percentage of the saturation curves at the temperature in question. Thus at 100° F. the value of H at 50 per cent humidity equals (0.50) (0.0426) = 0.0213. It has been emphasized that per cent humidity is not the same as per cent *relative* humidity. Inasmuch as data in the literature may be given as per cent relative humidity, it is desirable to convert such units into the units of humidity as used throughout this book.

Since per cent relative humidity is defined as

$$100\frac{p}{p_s},$$

and per cent humidity equals

$$100\frac{\dfrac{p}{760-p}}{\dfrac{p_s}{760-p_s}},$$

the factor by which the former must be *multiplied* to convert it to the latter is

$$\frac{760-p_s}{760-p},$$

where p and p_s are expressed in millimeters of mercury. Obviously this factor is never greater than unity. For example, air of 50 per cent relative humidity at 100° F. has a humidity of 48.4 per cent.

2. Specific Volume (Dry Air).—This quantity is calculated from the gas laws. (See pp. 4 to 7.) These state that the pound mol of air (29 lbs.) occupies 359 cu. ft. at standard conditions, namely, 492° F. abs. (32° F.) and normal barometer. Hence

$$\text{spec. vol.}=\frac{(359)\quad(t+460)}{(29)\quad(492)}=11.57+0.0252t,$$

where t is in ° F. It is clear that the specific volume increases linearly with t, as shown in Fig. 102. Thus at 100° F. the specific volume equals 14.09 cu. ft. per lb. of dry air.

3. Saturated Volume, and Humid Volume.—As defined, the *saturated* volume is on a basis of one pound of dry air, and equals the sum of the specific volume of the dry air plus the volume of the water vapor associated with the particular saturated mixture. The weight of the water vapor in saturated air at 100° F. is seen from the 100 per cent humidity line to be 0.0426 pounds, and the corresponding volume equals

$$\frac{(0.0426)\ (359)\ (460+100)}{(18.02)\qquad(492)} = 0.967 \text{ cu. ft.}$$

The saturated volume at 100° F. is then 14.09+0.97=15.06. A curve of such values is shown in Fig. 102.

Since *humid* volume is defined as the volume of any mixture, expressed as cubic feet of mixture per pound of dry air, and both the specific and saturated values are on the basis of one pound of dry air, the humid volume for any per cent humidity may be obtained directly by interpolation between the curves for specific and saturated volumes. For example, air of 50 per cent humidity at 100° F. has a humid volume of

$$(0.50)14.09+(0.50)15.06=14.58:$$

An interpolation on the chart will check this figure.

4. Latent Heat of Vaporization, r.—This value, expressed as B.t.u. per lb. of water evaporated, is found to decrease as temperature rises as shown in Fig. 102.

5. Humid Heat, s.—By definition,

$$s=0.238+0.48H, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and it is obvious that it should be plotted versus the actual humidity of the air, and it is so shown in Fig. 102. For example, the value of s for air, 50 per cent saturated at 100° F. ($H=0.0213$) is $0.238+(0.48)\ (0.0213)=0.248$. For saturated air at 100° F. ($H=0.0426$), $s=0.238+(0.48)\ (0.0426)=0.258$. In Fig. 102 the scale for s is shown at the top of the plot, and it should be noted that s is the only variable not plotted against temperature.

6. Adiabatic Cooling Lines.—On the humidity chart (Fig. 102) are shown certain lines starting at the 100 per cent humidity line

and running downwards to the right. These lines are called "adiabatic cooling lines." They afford a graphical solution of the problem of determining the relation between the initial and final condition for air, for "adiabatic evaporation."

A process is said to be "adiabatic" when heat interchange with the surroundings is negligible. Since, in many processes of drying and humidification substantially these conditions are found, equations for adiabatic operation are of value. The mechanism of vaporization of water exposed to warmer air will now be discussed.

When unsaturated air is passed over water colder than the air, the air temperature falls and under adiabatic conditions the sensible heat given up by the air is consumed in bringing the water to the wet bulb temperature and in evaporating water, thus humidifying the air.

If the water is initially at the wet bulb temperature, the mathematical statement of the heat balance, on the basis of 1 lb. of dry air, is as follows, in English units:

$$r_w dH = -s dt, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where dH is the differential weight of water (in pounds) evaporated into the air in cooling a differential amount dt (° F.) in temperature; s is the humid heat of the air, and r_w the heat of vaporization of the water at the wet bulb temperature in B.t.u. per lb. (The minus sign indicates that as H rises, t falls.)

Rearranging the above cooling equation for the adiabatic evaporation of water at the wet bulb temperature into air, one obtains:

$$\frac{dH}{dt} = -\frac{s}{r_w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which states that the slope of the curve of humidity with respect to air temperature is equal to the ratio $-s/r_w$, the minus sign indicating that the angle with the horizontal lies between 90 and 180°, *i.e.*, running downwards to the right.

For the special case in which the increase in humidity is small, the quantity, s, may be considered constant, and substantially equal to the humid heat of the initial air. Since r_w is also practically constant this means that the curve of H plotted against t is a curve of substantially constant slope, *i.e.*, a straight line.

The equation of this line is obtained by integration of this differential expression, giving,

$$H = -\frac{st}{r_w} + \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is an experimentally determined fact that when water evaporates into air adiabatically the process goes on until the air cools to the temperature of the water. Furthermore, this water temperature is, as indicated above, the wet bulb temperature of the air. This wet bulb temperature remains substantially constant throughout the process. Therefore, the end point of the process is obtained when the temperature of the air has fallen to its wet bulb point. Inserting therefore the limits H_w and t_w one obtains,

$$H = -\frac{st}{r_w} + H_w + \frac{st_w}{r_w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

A mathematical discussion and proof of these relationships will be found on pp. 458 to 461.

Inspection of Eq. (6*a*), which represents the process of adiabatic cooling of unsaturated air by contact with water at its wet bulb temperature, shows that the air falls in temperature and rises in humidity along a path which is represented by a straight line in the humidity chart (Fig. 102). Furthermore, the slope of any such line is equal to the humid heat of the initial air divided by the heat of vaporization of water at the wet-bulb temperature. Since humid heat increases with the humidity of the air, the higher the humidity of the initial air subjected to such a cooling process, the steeper the cooling line. Similarly, since heat of vaporization decreases as temperature rises, the higher the wet-bulb temperature of the process, the higher the slope. For any specific case the numerical value of the slope is obviously determined by these two factors. In order to make it possible to obtain graphically the slope corresponding to any case that may arise within reasonable limits of industrial practice, there are drawn on Fig. 102 a series of cooling lines. Each of these lines starts at its right-hand end at a certain humidity, corresponding to its ordinate at that point. The line ends on the 100 per cent humidity curve at the wet-bulb temperature. Its slope is drawn to correspond

to the proper value of s/r_w determined by these initial and final conditions.

To illustrate how the slope of any particular line is determined from the initial and final conditions, calculate the slope of the adiabatic cooling line for air with a humidity of 0.0130, *i.e.*, with a dew point of 65° F., cooling to a wet bulb of 95° F. The humid heat of the entering air, as read from the humid-heat line on the diagram, is $0.244 = s$. The heat of vaporization of water at 95° F. (the wet-bulb temperature) is 1048 B.t.u. $= r_w$. The ratio of the two, 0.000233, is the slope of the cooling line. The slope of the cooling line for this case on the chart will be found to check this figure.

At high temperatures a group of these cooling lines starts from a common wet-bulb point, all of the group corresponding to the single wet-bulb temperature but different initial humidity. Thus for the wet-bulb temperature of 95° two lines are shown, the one just calculated starting at an initial humidity of 0.013 and a second, corresponding to an initial humidity of 0.0027. At lower temperatures the possible variations in humidity are so small that appreciable variations in slope cannot be caused thereby, and consequently only one line is drawn for each wet-bulb point. Hence, where air cools itself adiabatically through contact with water at its own wet-bulb temperature, the temperature falling until it is equal to that of the water itself, the process is represented on the humidity chart by the cooling line which starts at its right-hand end at the initial humidity of the air and ends at its left-hand end at the wet-bulb temperature. If no cooling line which exactly meets these conditions is shown on the chart, the actual operating line will start at the actual initial humidity and run to the saturation curve substantially parallel to that cooling line shown on the diagram whose initial humidity and final wet-bulb temperature most nearly equal those corresponding to the operating conditions.

Usually, however, the air does not cool completely to the wet-bulb temperature, as assumed in the preceding paragraph. For this case a heat balance shows that

$$(H_2 - H_1)[(r_w + 0.48(t_2 - t_w)] = s_1(t_1 - t_2), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where the subscripts 1 and 2 correspond to the initial and final conditions. From inspection of this equation it is clear that the

slope of the cooling line on the humidity chart which represents this change is equal to

$$\frac{s_1}{[r_w+0.48(t_2-t_w)]}.$$

The cooling lines were drawn with a slope corresponding to the initial humidity. Consequently, therefore, the only difference in slope is due to the correction term to r_w in the denominator. Except where the wet-bulb depression at the end of the operation is high, this correction term is negligible. If it be desired to correct for this factor, it will be noted that the denominator is equivalent to a heat of vaporization at a somewhat lower temperature. Since the heat of vaporization changes roughly 0.6 B.t.u. per degree, the proper slope can be obtained by using a cooling line whose wet bulb is below the actual wet bulb by an amount approximately 0.8 of the wet-bulb depression at the end of the operation.

Inasmuch as the chart is drawn for a constant, total pressure of normal barometer, whereas the actual pressure in the apparatus in question may be slightly greater or less, and since heat interchange with the surroundings is not always entirely negligible, it is not worth while to go into these refinements. For the same reason, slight changes in data for the latent heat, specific heat, and vapor pressure are immaterial.

Choice of Adiabatic Cooling Line for Adiabatic Cooling.—If any air mixture of known composition and initial temperature cools itself by adiabatic evaporation to a known final temperature, the exact condition reached may be graphically determined by drawing a straight line, starting at the initial temperature and humidity, parallel to that cooling line, the lower right-hand end of which starts at a humidity equal to that of the air at the beginning of the cooling process, and which ends at the wet-bulb temperature of the process.

In case a cooling line exactly fulfilling these requirements cannot be found on the chart, the proper slope can be estimated with ease by interpolating between the lines most nearly meeting the requirements, because of the fact that the variation in slope of these lines is so slight, the lines for all cases being nearly parallel. In the solution of problems in which the exact initial condition and

the exact final temperature of the cooling process is not known, it is sometimes necessary to estimate these quantities so as to make possible the choice, as first approximation, of one of the cooling lines. Such an estimation will so nearly determine the initial and final conditions that a second choice of cooling line will without fail be sufficiently accurate for the determination of the proper slope.

Use of Adiabatic Cooling Lines for the Determination of Humidity by Wet and Dry Bulb Thermometer Readings.—A quantitative relation between the wet and dry bulb temperatures and the actual partial pressure of water in air has been previously derived (pp. 444 to 445). As shown on pp. 458 to 461 the relation between the wet and dry bulb temperatures (t_w and t_a) and the humidity (H_a) of the air is given by the following equation:

$$H_a=-\frac{st_a}{r_w}+\text{constant}=-\frac{st_a}{r_w}+H_w+\frac{st_w}{r_w},$$

which is identical with Eq. (6*a*) used above to construct the adiabatic cooling lines in Fig. 102. Hence, the adiabatic cooling lines in Fig. 102 may be used, not only for the purpose previously explained, but also to determine the relation between humidity and wet and dry bulb readings.

Choice of Adiabatic Cooling Line for Wet and Dry Bulb Thermometry.—Inasmuch as the wet bulb temperature of the air is the final point of adiabatic evaporation of water into air, these same cooling lines may be used to determine the humidity of air from the wet and dry bulb readings. Call the wet bulb temperature t_w, and the temperature of the entering air t_a. On the temperature scale of the plot find the point corresponding to t_w, intersection with the 100 per cent saturation curve. From this point follow down to the right along a straight line parallel to one of the nearest cooling lines, choosing that cooling line whose lower end lies nearest the final humidity, until the abscissa of the dry bulb temperature, t_a, is reached. The ordinate of the point thus determined is the humidity, *i.e.*, the water content per pound of dry air of the mixture whose characteristics are t_w and t_a. The total carrying power of the air at t_a, is read directly from the saturation curve at the dry bulb temperature, t_a, and the actual humidity divided by this total carrying power is the percentage

humidity. Moreover, the curves of per cent humidity, drawn for every 10 per cent, may be used to determine this quantity by interpolation. For careful work, triangles should be used in following the directions of the cooling lines, but for approximate work estimation is satisfactory.

This diagram, representing as it does the condition of air-water vapor mixtures through the range ordinarily met in commercial practice, is superior to the psychrometric charts so frequently encountered. In the first place, unlike any system expressing humidity in terms of partial pressure, a change in

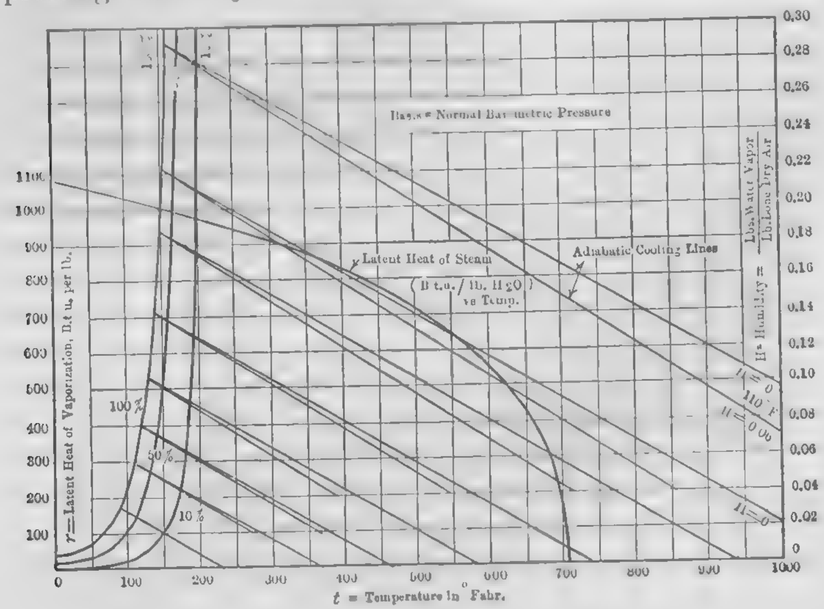


FIG. 103.—Humidity Chart, *High Range.*

temperature of the air involves no change in composition unless that change in temperature be accompanied by evaporation of water into the air or condensation of water from it. Therefore, any change consisting alone in a decrease of the temperature of the air must be represented by a horizontal line in the diagram until the saturation point is reached, when the saturation curve must be followed. Furthermore, the cooling lines represent adiabatic evaporation, and make possible the immediate estimation of the condition of the air from its wet and dry bulb readings. Also the absolute amount of moisture picked up or given up by a unit weight of air is determined immediately by the difference between the ordinates corresponding to its initial and final states.

Figure 103 is a humidity chart similar to the one previously described, except that here the ranges of humidity and temperature are far greater; it is useful in the solution of certain types of problems in drying, pages 532 to 533.

ILLUSTRATIONS SHOWING THE USE OF THE HUMIDITY CHART

Illustration 1.—Assume a drier in which 200 lbs. of water are evaporated hourly from the material being dried; the available air has a humidity of 0.0100 and a temperature of 75° F., and is heated to 155° F. before entering the drier. The air leaving the drier has a wet bulb temperature of 100° F. and a dry bulb of 130° F. No other assumptions are made as to the material being dried, nor as to the construction and operation of the drier. Calculate the air consumption.

Solution.—The air enters this drier as stated with a humidity of 0.0100. Its humidity on leaving the drier is obtained by following the cooling line starting at 100° F., the wet bulb temperature, down to the right to 130° F., indicating a final humidity of 0.0350. The rise in humidity of the air going through the drier is therefore the difference, or 0.0250. Hence this figure is the pounds of water picked up per lb. of dry air. Since the water evaporated per hour is 200 lbs., the air consumption per hour is 200 divided by 0.0250 or 8000 lbs. of bone-dry air.

Illustration 2.—Referring to the data in the preceding illustration, what was the volume of air before and after preheating?

Solution.—The air entering the preheater had a humidity of 0.0100 and a temperature of 75° F. Reference to Fig. 102 indicates that its per cent humidity entering the preheater was 55; interpolation between the curves for saturated volume and specific volume at 75° F. indicates that the humid volume (of the mixture of water vapor and dry air) was 13.70 cu. ft. per lb. of dry air at the entrance to the preheater.

The air leaving the preheater at a humidity of 0.0100 and a temperature of 155° F. had a per cent humidity of about 4; a similar interpolation at 155° F. indicates that the humid volume of the air leaving the preheater was 15.70 cu. ft. per lb. of dry air.

Other things being equal, the fan for forcing the air through the apparatus should be designed on the basis of the humid volume of the air *entering* the preheater, inasmuch as the fan should be placed where the air has the maximum density, because with a given volumetric capacity to the fan, the weight capacity is at a maximum when the air handled is coldest. Note that these calculations require no knowledge of the theory of the drying process itself, nor of the mechanism of the drier under consideration.

Illustration 3.—The water in the stock being dried in this apparatus entered the drier at 70° F. and the water vapor removed left the drier at 130° F. Calculate the B.t.u. per hour (*a*) supplied to the drier other than in the air entering at 155° F. and (*b*) that supplied by the preheater, neglecting [1]

[1] These quantities sometimes are considerable.

heat losses to the surroundings, and that necessary to warm up the stock and the conveying mechanism.

Solution.—Per pound of water evaporated the heat consumption is that necessary to warm the water from 70° to 130° F., or 60 B.t.u., plus that necessary to evaporate it at 130° F., or as read from the chart, 1023 B.t.u., a total of 1083 B.t.u. The heat utilized for evaporation, expressed per pound of dry air, is therefore, 1083×0.025 or 27.1 B.t.u. The heat given up per pound of dry air during its passage through the apparatus is equal to the drop in temperature (155–130°), times its humid heat (0.242), or 6.1 B.t.u. This quantity is less than the heat consumption, thus demonstrating that this drier is furnished with some sort of heat supply other than that of the drying air itself, and the difference between these two quantities, 21.0 B.t.u., is the heat furnished by the heating surface within the drier, expressed per pound of dry air. Since 8000 lbs. of dry air were consumed, the B.t.u. per hour furnished by the heating surface within the drier was 168,000.

Since the entering air was preheated from 75° to 155° F., a rise in temperature of 80°, the humid heat of this air being 0.242, the heat furnished by the preheater was the product of these two quantities, 19.4 B.t.u., expressed per pound of dry air; or the total was this times the amount of dry air per hour = 154,800 B.t.u.

Other Illustrations.—Additional illustrations of the use of the chart will be found in the chapter on Humidifiers, Dehumidifiers, and Water Coolers, and in the chapter on Drying.

DERIVATION OF EQUATIONS

For purposes of derivation of equations, assume a long tunnel through which unsaturated air is flowing at constant mass velocity. The walls of this tunnel are non-conductors of heat. Along the bottom of the tunnel is placed a mat or wick permanently wet with water supplied from below as evaporation takes place above. The water is furnished to this wick at every point at a temperature exactly equal to that of the water on the upper surface of the wick at that point. There is no motion of the liquid water parallel to the axis of the tunnel. The mass velocity of the air over the water is constant and sufficiently low so that heat generated by friction may be neglected.

The unsaturated air entering this tunnel will become humidified as it passes through it owing to evaporation of water. In consequence the temperature of the air will fall and if the tunnel be sufficiently long the water and air will ultimately come to equilibrium.

Now consider for the moment the conditions at any definite point along the length of this tunnel. At this point the temperature, humidity, and pressure of water vapor in the air will be represented by t, H, and p. Since the apparatus is continuous in its operation these conditions will remain unchanged at this particular point, but will vary from point to point along the tunnel. The corresponding quantities representing the condition of the

liquid water in contact with the air film at this particular point are t_w, H_w, and p_w.

The mechanism of interaction of the water with the air is as follows: There exists over the water what is equivalent to a stationary film of air,[1] which insulates the water from the main body of the air. Through this air film heat is diffusing from the air into the water, and through the same film there is diffusing in the opposite direction, the water, vapor formed by evaporation on the surface of the liquid. This evaporation cools the surface of the water, and, since it is available from no other source, heat must be supplied solely by diffusing from the air. The heat of vaporization must, therefore, be quantitatively compensated by the heat flow through the surface film, and the rate of evaporation is limited by the rate of diffusion of vapor through the same film.

From the above one can write the following equations:

$$-\frac{dW}{Ad\theta}=k(p_w-p) \quad . \quad (1); \qquad \frac{dq}{Ad\theta}=h(t-t_w) \quad . \quad (2); \qquad dq=-r_w dW \quad . \quad (3);$$

Whence

$$p_w-p=\frac{h}{kr_w}(t-t_w) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For nomenclature used in this derivation, see p. 461. This last equation is the one normally used for calculating the humidity of air from wet and dry bulb thermometer readings. In it variation in r_w is neglected and the term h/kr_w is assumed constant. The equation implicitly assumes that the cooling of the air is *differential*, *i.e.*, so small in the neighborhood of the point in question that the actual changes in temperature and humidity of the air, t and p (*or* H) are negligible.

It is obvious that h and k depend on the effective thickness of the air film and are therefore functions of the velocity of the air. It is, however, equally obvious that, if air velocity be increased sufficiently to double the one, the other will double also. The ratio of h/k therefore remains constant, independent of velocity. This explains why the reading of a wet bulb thermometer is uninfluenced by the velocity of air passing it, provided the velocity is sufficient so that any heat lost by radiation is negligible in comparison with that picked up by conduction. Since

$$p=P\frac{H/18}{H/18+1/29}^{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$t-t_w=\frac{kr_a}{h}P\left[\frac{H_a/18}{H_w/18+1/29}-\frac{H/18}{H/18+1/29}\right] \quad . \quad . \quad . \quad . \quad (6)$$

[1] See Fluid Films, pp. 36 to 41.

[2] This involves the assumption, entirely valid under normal conditions, that the water vapor follows the gas laws. The deviations from the gas laws become progressively less as pressure decreases; even at the saturation pressure at 150° F. the deviation is less than 0.7 per cent.

Where H is small, as is usually the case below 150° F., $H_w/18$ and $H/18$ are negligible compared with 1/29, and one may write as a close approximation,

$$t-t_w=\frac{k'r_w}{h}(H_w-H), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $k'=29k\,P/18$.

Now consider the change in humidity and temperature of the air as it moves along the tunnel. Starting at the same point previously considered, the air will drop in temperature by an amount dt and increase in humidity by an amount dH. The heat given up by the cooling must correspond to the heat of vaporization of the water picked up, *i.e.*,

$$-s\,dt=r_w\,dH,^1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

whence, assuming constancy of s and r_w,

$$H=-\frac{st}{r_w}+\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Assuming the tunnel indefinitely long, the air will ultimately become saturated at some temperature t_e, and humidity H_e. Since these conditions represent equilibrium between the air and the water, evaporation will cease, and t_e and H_e are therefore the constant, fixed end points of the process. Inserting these limits in Eq. (8) one obtains:

$$H_e-H=\frac{s}{r_w}(t-t_e). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Two equations connecting H and t have been derived, both applying to this same process of evaporation, namely:

$$H_e-H=\frac{s}{r_w}(t-t_e) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$H_w-H=\frac{h}{k'r_w}(t-t_w). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

These two expressions must therefore be identical. By the method of undetermined coefficients this can be true only providing the corresponding coefficients are equal, namely:

$$\frac{h}{k'r_w}=\frac{s}{r_w}, \quad \text{or} \quad \frac{h}{k'}=s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$t_e^{\,1}=t_w, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$H_e=H_w. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

[1] The exact form of this equation is

$$-s\,dt=[r_w+0.48\ (t-t_w)]dH.$$

In Eq. (8) the correction term to r_w is neglected.

[2] W. H. Carrier, *J. Am. Soc. Mech. Eng.*, 34, 1309 (1911), stated as a general principle, that the wet bulb temperature of air remains constant during "adiabatic" evaporation of moisture into it. However, he gave no proof or adequate explanation of the statement. From this derivation it is obvious that the statement is true only where the amount of vapor in the air is small, *i.e.*, this relationship represents merely a limiting case. With high vapor concentration the wet bulb temperature changes during such a process. The variation is, however, negligible for almost all engineering work.

Equation (12) states that the end point (t_e) of adiabatic evaporation of water into air is the wet bulb temperature (t_w).

Since Eqs. (10) and (7) are equal, it has been shown that the adiabatic cooling lines on the chart, Fig. 102, which are calculated from Eq. (10), may be used for determining:

(*a*) the humidity of air, knowing the wet and dry bulb temperatures, and

(*b*) the relation between the initial and final conditions of air for adiabatic evaporation.

Equation (11) states that the coefficient of heat transfer (h) *through the gas film* divided by the coefficient of vapor diffusion (k') through the same gas film is a constant for any given conditions, and equal to the humid heat of the gas. The importance of this relationship is very great in problems involving the transfer of heat or matter by the process of diffusion. For if the heat transfer coefficient for a certain type of apparatus operating under definite conditions is known, the capacity of this same apparatus may be predicted when functioning as a gas scrubber. Conversely, if k' is known, one can predict h.

Nomenclature for Derivations

A = Surface area of liquid in contact with gas.
H = Humidity of gas, parts by weight of vapor per part by weight of vapor-free gas.
h = Film coefficient of heat transfer between gas and liquid, heat units per unit time per unit surface area per unit temperature difference.
k = Coefficient of diffusion, parts by weight of vapor diffused per unit time per unit area per unit *vapor pressure* difference.
k' = Coefficient of diffusion, parts by weight of vapor diffused per unit time per unit area per unit *humidity* difference.
p = Partial pressure of vapor.
P = Total pressure of vapor and vapor-free gas (*i.e.*, barometer).
q = Number of heat units transferred.
r = Latent heat of vaporization, heat units per unit weight of liquid vaporized.
s = Humid heat, number of heat units necessary to change the temperature of unit weight of vapor-free gas *plus the vapor it contains*, one degree.
t = Temperature.
θ = Time.
W = Weight of liquid evaporated.

CHAPTER XV

HUMIDIFIERS, DEHUMIDIFIERS, AND WATER COOLERS

The equilibrium relationship in a system comprised of water, water vapor and air, and the temperatures reigning in such a system, form the basis of certain types of apparatus much employed in industrial work. The more important are included under the descriptive terms, humidifiers, dehumidifiers, and water coolers.

GENERAL CONSIDERATIONS

Humidifiers.—When it is desired to increase the humidity of air or other gas, live steam may be blown into it. However, this increases the temperature and it is difficult to control the humidity; consequently it is generally more satisfactory to bring the air into contact with liquid water.

When the air entering an enclosure containing water is unsaturated and warmer than the water, heat is transferred from the air to the water, thus lowering the temperature of the air; this heat is largely consumed in vaporizing water, which diffuses into the air, increasing its humidity. Such a process is called "Humidification," "Air-cooling," or "Air Washing."

In a humidifier where surface is provided either by the use of a water spray or by allowing water to trickle over suitable packing, a relatively large amount of water must be circulated in order to maintain the wet surface. At ordinary temperatures the rate of evaporation from such a surface is small so that only a small percentage of the water circulated is evaporated per cycle. As shown on p. 460, water in contact with air assumes the wet bulb temperature of that air and it is therefore obvious that the water recirculated in a humidifier will be at all points at substantially the wet bulb temperature unless the temperature of the small amount of make-up water used is widely different.

Even when the water fed into the apparatus is not at wet bulb temperature it reaches this temperature in a very short time.

Figure 104 shows a typical spray chamber as used for humidification. The air enters through the inlet dampers and passes through the preheating coils into the spray chamber. In this particular case the flow of air and water is parallel. The air leaving the spray chamber passes through the eliminators or baffles, which may be kept wet by flooding nozzles. The air then passes into subsequent apparatus, sometimes through re-heating coils as shown. Usually such apparatus is automatic in action, the control depending on the readings of wet and dry bulb thermometers, or upon the "dew point" of the exit air.

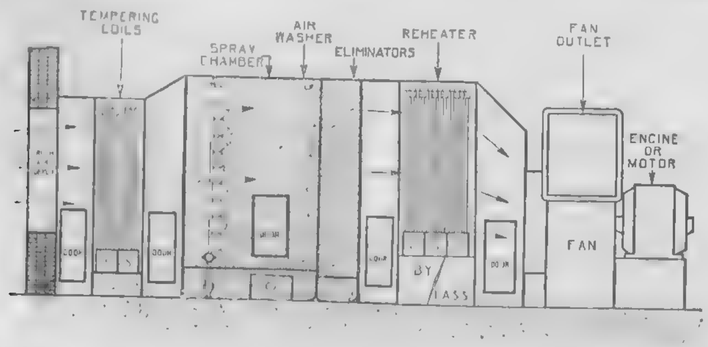


FIG. 104.—Sturtevant Horizontal Spray Type Humidifier, or Air Washer.

Figure 107, p. 474, shows another type of apparatus which may be used for humidification.

Humidifiers are used widely in ventilating practice, and are finding extensive use for humidifying air for "conditioning" rooms in which certain materials, such as textiles, are allowed to regain moisture removed at some previous step in the process, or where the moisture in the stock must be kept at a predetermined figure.

Dehumidifiers.—It is sometimes necessary to remove moisture from air. Where complete removal is not required it is usually most satisfactory to dehumidify by cooling and condensation rather than by adsorption or chemical absorption. The cooling can be brought about by ordinary pipe coolers but in such a case the heat transfer coefficient is small, thus requiring a large amount of an expensive type of cooling surface. Instead of using a pipe cooler directly, the result can be accomplished more cheaply by the

use of two pieces of apparatus: *first*, a spray chamber, or similar apparatus, in which cold water is brought into direct contact with the air; *second*, a double-pipe cooler in which the water is cooled by refrigerated brine. The first of these is very cheap, and the second, while of an expensive type, need not be large, because of the relatively high coefficient of heat transfer from water to brine in the pipe cooler.

When saturated air is brought into contact with water colder than itself, the *sensible* heat content of the air is reduced by heat transfer to the water, and water vapor diffuses from the saturated air into the colder water, the heat liberated by *both* mechanisms being consumed in raising the temperature of the water. Since such a process decreases the humidity of the air, it is described as "*Dehumidification.*"

Dehumidifiers are used in ventilating work when it is more economical to dehumidify air already used than to heat and humidify cold air from outdoors. They are also used in connection with driers in which air is recirculated. (See p. 493.)

Water Coolers.—When water comes in contact with air the wet bulb temperature of which is lower than the temperature of the water, the water is rapidly cooled by evaporation. If this unsaturated air is cooler than the water with which it is brought into contact, the water is cooled not only by evaporation but also by the transfer of sensible heat to the air.

Water coolers are employed in engineering practice where cooling water is scarce. The forms ordinarily used are Cooling Towers and Spray Ponds. Figure 105 shows one type of water cooler.

To recapitulate, the humidity increases in a humidifier, decreases in a dehumidifier, and increases in a water cooler; the water temperature is practically constant in a humidifier, rises in a dehumidifier, and falls in a water cooler; the air temperature falls in the first and second and usually rises, but may fall, in the third.

METHOD OF CALCULATION

The humidity chart discussed in the preceding chapter is used for determining the relation between the initial and final temperatures and humidities of the air. Knowing these terminal conditions, one can readily determine the stoichiometric relation

between the amount of air handled, the change in humidity, and the water evaporated or condensed. Examples of such calculations are given on pp. 474 to 478.

The size of a humidifier or dehumidifier for a given capacity and operating conditions may be calculated by the use of either of two equations: one, depending on the transfer of *sensible* heat from the air to the water surface, and the other, depending on the

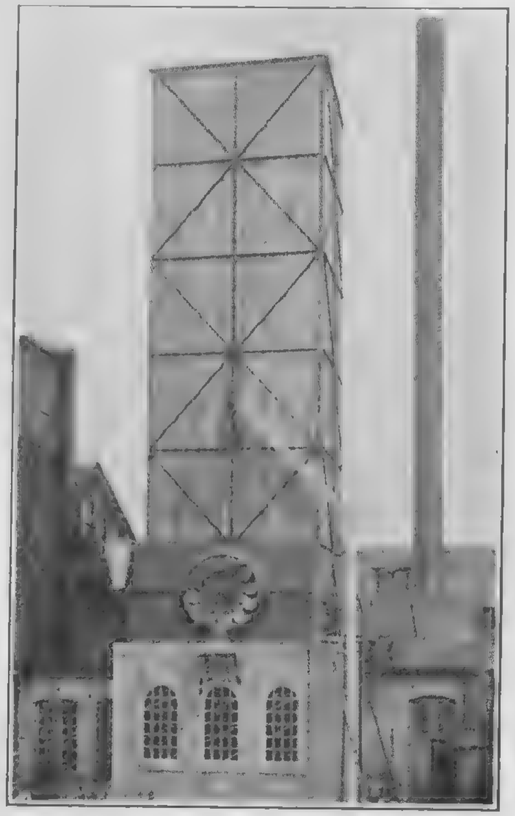


FIG. 105.—Wheeler Cooling Tower.

diffusion of water vapor from or to the air, to or from this same water surface.

The heat effect due to evaporation or condensation is disregarded in the heat transfer equation, except as it influences the water temperature and hence the average temperature difference between water and air. Both of these processes, heat transfer and diffusion, take place simultaneously and the coefficients of the two equations are tied together by a very simple relation;

hence the apparatus may be designed on the basis of either mechanism. In calculations for humidification and dehumidification, the heat transfer equation is more convenient than the diffusion equation, but both must be used for water coolers.

Nomenclature

G = Lbs. of bone dry air per minute passing through the apparatus.
H = Humidity of air, as lbs. of water vapor per lb. of bone-dry air.
H_w = Humidity of water face of air film on the water surface = humidity at saturation at water temperature.
ha = Overall coefficient of *sensible* heat transfer, expressed as B.t.u. per min. per ° F. per active cu. ft. (h = B.t.u. per min. per ° F. per sq. ft. of transfer surface, and a = sq. ft. of transfer surface per active cu. ft.)
$k'a$ = Overall coefficient of vapor diffusion, expressed as lbs. per min. per active cu. ft. per unit $H_w - H$.
Q = *Total* heat change, B.t.u. per min.
q = *Sensible* heat change in air, as B.t.u. per min.
R = Rate at which water enters apparatus, as pounds per minute.
r = Heat of vaporization of water, B.t.u. per lb. See Humidity Chart for values.
r_w = Value of r at wet bulb temperature.
s = Humid heat of air. See Humidity Chart for values.
t = Temp. of air in ° F.
t_w = Wet bulb temperature of air, ° F.
T = Temp. of water in ° F.
V = Active volume of apparatus in cu. ft., *i.e.*, the volume in which air and water are in contact. Ordinarily taken as total volume of apparatus, corrected for liquor storage space, etc.
w = Lbs. of water vapor diffusing per minute.

Subscripts.—1 refers to conditions of *both* liquid and gas at the *gas entrance*, and 2 to the *gas exit*.

Equations for Humidification.—Since humidification as carried out in industrial practice is substantially an adiabatic cooling process, the relation between H and t is given by an adiabatic cooling line on Fig. 102. The following heat transfer equation[1] shows the relation between size, capacity and temperatures of air and water:

$$q = Gs_1(t_1 - t_2) = haV(t - T)_{av}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] For derivation, see pp. 478 to 480.

The mean value of the overall temperature difference from air to water, $(t-T)$, or Δt, is the *logarithmic* mean:

$$(t-T)_{av} = \frac{\Delta t_1 - \Delta t_2}{2.3 \log_{10}\left(\frac{\Delta t_1}{\Delta t_2}\right)}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

However, the arithmetic mean,

$$(t-T)_{av} = \frac{\Delta t_1 + \Delta t_2}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

gives a value checking the logarithmic mean within 4 per cent when Δt_1 is not more than twice Δt_2. Hence, when so low a ratio of temperature differences prevails, one may use the arithmetic mean without introducing serious error. Values of the coefficient ha will be given later.

The water evaporated may be calculated in two ways:

$$w = \frac{q}{r_w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$w = G(H_2 - H_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Usually, greater precision is obtained from Eq. (3) than from Eq. (4). In humidification, w is equal to the " make-up " water.

In order to show the results of tests of a humidifier graphically, an equivalent form[1] of Eq. (1) may be used:

$$\frac{t_2 - T_w}{t_1 - T_w} = e^{-haV/Gs}. \quad . \quad . \quad . \quad (5)$$

This equation states that if the air be flowing at constant rate (pounds per minute) through an enclosure in which it comes in contact with water, the total surface of which is kept constant, the ratio of the temperature of the exit air less its wet

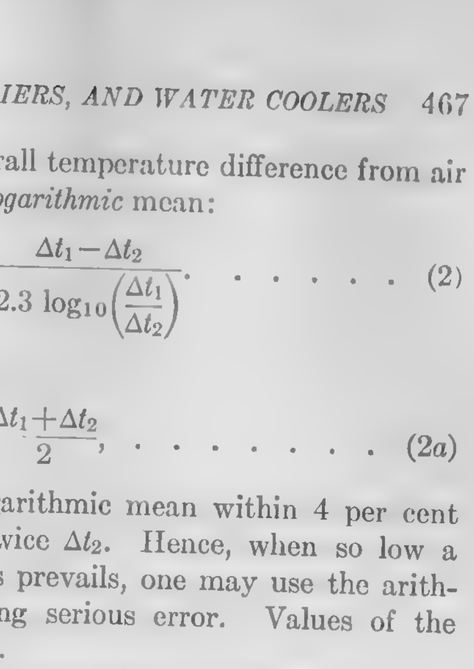


Fig. 106.—Humidifier Data.

[1] The derivation of this form of Eq. (1) is given on pp. 478 to 480.

bulb reading to the temperature of the entering air less its wet bulb value is a constant, $e^{-haV/Gs}$, whatever the temperature of the entering air may be. Where G is held constant in a given apparatus, ha will be constant, and hence one may plot (t_1-T_w) versus (t_2-T_w), and from the slope of the line determine the value of ha. See Fig. 106.

Equations for Dehumidification.—This term will be used herein only where the air entering the apparatus is saturated. The relation between H and t is then given by the 100 per cent humidity curve on Fig. 102, p. 448. For such conditions, as in the case of humidification,

$$q=Gs_{av}(t_1-t_2)=haV\,(t-T)_{av}. \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

The arithmetic average of the initial and final humid heats will be used for s_{av}. As will be shown later, the value of the overall coefficient ha is *less* for dehumidification than for humidification.

The water *condensed* may be calculated as follows:

$$w=\frac{Q-q}{r_{av}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

Or,

$$w=G\,(H_1-H_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Usually, greater precision is obtained from Eq. (3a) than from Eq. (4).

For counter flow of air and water (the usual arrangement), the relation between the rate of flow (R) of entering water, the rise in water temperature (T_1-T_2), and the total heat evolved (Q) is as follows:

$$Q=R(T_1-T_2)=wr_{av}+Gs_{av}(t_1-t_2) \quad . \quad . \quad . \quad . \quad (6)$$

Equations for Humidification plus Dehumidification.—If the entering air is not saturated, it will first cool to saturation. After dehumidification begins the relation between H and t is given by the 100 per cent humidity curve on the chart.

The process always involves a number of stages,[1] each of

[1] If the cooling water in contact with the air be at a temperature *below* its dew point the air is dehumidified by diffusion of water vapor into the water and simultaneously cooled by abstraction of heat by conduction. Both these mechanisms tend to increase the temperature of the water.

If the temperature of the cooling water be *above* the dew point but below that of the air, water evaporates into the air but the air is cooled by conduction as before. Evaporation tends to cool the water, but conduction tends to heat it.

At the wet bulb temperature these two tendencies balance. If the temperature of the water in contact with air be above that of the air itself the water is cooled both by evaporation and by conduction of heat. In the quantitative analysis of any specific case the two processes occurring simultaneously must be considered separately.

which must be considered separately, involving different values of ha, $(t-T)_{av}$, and q in each stage.

Equations for Water Coolers.—Obviously *counterflow* of air and water will be used. One relation immediately available is a heat balance:

$$Q=Gs_{av}\,(t_2-t_1)+G\,(H_2-H_1)\,r_{av}=R\,(T_2-T_1), \quad . \quad . \quad (6a)$$

where arithmetic mean values for s and r are taken.

As for humidifiers and dehumidifiers, the *sensible* heat transfer may be calculated according to the following equation:

$$q=Gs_{av}(t_2-t_1)=haV\,(T-t)_{av}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

Since the ratio of the initial and final values of $T-t$ is generally small, the arithmetic mean temperature difference usually gives sufficient precision:

$$(T-t)_{av}=\frac{(T_1-t_1)+(T_2-t_2)}{2} \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

As previously indicated, the water vapor diffuses through the same water surface by a parallel process:

$$w=G\,(H_2-H_1)=k'aV\,(H_w-H)_{av}, \quad . \quad . \quad . \quad . \quad (7)$$

where $k'a$ is the diffusion coefficient, and H_w-H is the difference in potential, or "humidity driving force." (H_w is the humidity of the water face of the air film on the water, while H is the humidity of the main body of air at the same section of the apparatus.) Under most conditions met in practice the arithmetic mean gives sufficient precision:

$$(H_w-H)_{av}=\frac{(H_w-H_1)+(H_w-H_2)}{2} \quad . \quad . \quad . \quad . \quad (8)$$

It should be noted that in a water cooler, the water temperature, and hence H_w, *varies* throughout the apparatus. In designing

a water cooler, the initial and final water temperatures (T_2 and T_1) and the rate of input (R) of the water are known, as is the initial temperature (t_1) and humidity (H_1) of the available air. Furthermore, data for the coefficients ha and $k'a$ are available for towers of certain types. Hence, with the three equations given above, and the humidity chart, it is possible to calculate the amount of air required, the volume of the apparatus, and the temperature and humidity of the air leaving the water cooler. As a first approximation, the temperature of the air leaving the apparatus may be taken as 5 to 10° F. below that of the entering hot water. This trial value must later be checked against values required by the equations used.

Discussion of Overall Coefficient *ha*.—The following points should be kept clearly in mind:

1. The coefficient ha is obtained experimentally and is expressed as B.t.u. (*as sensible heat only*) per minute per ° F. *average overall* temperature difference per cu. ft. Although ha can be determined by experiment, it consists of two factors, neither of which can conveniently be determined separately. A possible exception to this last statement is found in certain packed towers where it is possible to estimate the term a, *i.e.*, the total sq. ft. of wetted surface per cu. ft. of tower. The exact value of the *overall* coefficient of heat transfer cannot, in general, be predicted for apparatus for humidification, dehumidification, and the like, but the qualitative effect of changing certain variables, such as velocity of gas or liquid, may be predicted in certain cases.

2. Since the term a represents the sq. ft. of active surface per cu. ft. of active volume of apparatus, it will vary widely with the type or design of the apparatus. Even in a definite type of apparatus, gas velocity, rate of liquor circulation, or both, undoubtedly affect the active surface per unit of volume.

3. In addition to this, as brought out repeatedly in the chapter on "Flow of Heat," changes in velocity and viscosity have marked effects on certain film coefficients of heat transfer, and hence on the overall coefficient.

All of these facts make the estimation of values of ha extremely difficult, and hence for accurate design it is necessary to determine the coefficient for the particular conditions under consideration. However, by having a clear insight into the nature of the variables which determine ha, the amount of experimental work required may

be reduced to a minimum. While the designing of apparatus of these types in the absence of preliminary experimental work is undesirable, yet the problem sometimes arises, and here one must interpret the results of experiments in similar apparatus with care and employ suitable factors of safety.

Application of Film Concept and Potential Concept.—This procedure is used by Whitman and Keats,[1] who employ the following nomenclature:

ha_H = *Overall* coefficient of heat transfer for *humidification*.
ha_D = *Overall* coefficient of heat transfer for *dehumidification*.
ha_G = *Film* coefficient of heat transfer through *gas* film.

Unless otherwise stated the liquid involved is water.

As previously indicated,[2] in *humidification* the heat flows from the air through the air film to the outer surface of the drop, while water vapor diffuses through this film into the air, the water temperature remaining unchanged. Since the heat does not penetrate into the water itself in this case, the only resistance here is that of the gas film, hence

$$ha_H = ha_G \quad \ldots\ldots\ldots\ldots (9)$$

In the process of *dehumidification*, the heat flows not only through the gas film but must also penetrate into the drop, as the water becomes warmed in the process. The process of dehumidification is complicated. The sensible heat removed from the air must travel in series through both the gas and the liquid films, but the latent heat of condensation is liberated at the interface between the films and as heat travels through the liquid film only. The vapor condensed must travel, however, by diffusion through the gas film, and there must be a partial pressure gradient through this film sufficient to cause the diffusion. The quantitative interrelationships can be derived by the methods used on pages 458 to 461, but the meagre data available have not been analyzed in this way.

Data giving direct experimental determinations of the overall coefficients, ha_D and ha_H, in four distinct types of apparatus for varying conditions of air and water velocity are tabulated and discussed on the following pages. The value of ha_D there given are based on sensible heat only.

[1] *J. Ind. Eng. Chem.*, **14**, 186 (March, 1922).
[2] See pp. 413 and 441.

DATA—VALUES OF THE OVERALL COEFFICIENT (ha)

Note.—All values of ha are given as B.t.u. (sensible heat) per minute per ° F. per cu. ft. of active volume.

Horizontal Spray Chamber.—Tests on a four-stage counter-flow horizontal spray chamber gave the following values:

Air Velocity. Lbs. of dry air per min. per sq. ft. of cross-section	Humidification (ha_H)	Dehumidification (ha_D)
22.7	1.39	0.359
28.0	1.73	0.409
35.6	1.67	0.403
41.9	1.47	0.428
45.3	1.47	0.495
Average.....	1.55	0.42

The above values were determined with a spacing of 7 ft. from bank to bank and 1.78 sprays per sq. ft. of cross-section, hence there were 3.93 cu. ft. of chamber per spray. The water rate per spray was held constant at 12.5 lbs. per minute per nozzle, the pressure on the nozzles being 22 lbs. gauge. The amount of water sprayed per nozzle is quite important, as well as the spacing of the sprays and spacing of the banks. While water temperature is probably important in determining ha_D, theoretically it should not affect ha_H, as only the gas film is involved in the latter case.

Tests on two other spray chambers of different design gave values of ha_H of 1.1. and 1.5.

As shown by recent experiments of Robinson and Roll[1] on a commercial, horizontal, one-stage spray humidifier with parallel flow of air and water,

$$ha_H = 0.0592\ (n)\ (r)^{1.57},$$

[1] M. I. T. Thesis, 1921. These constants must be determined for each design of nozzle.

where n varied from 0.785 to 1.57 nozzles per sq. ft. of cross-section, r varied from 3 to 8.5 lbs. of water per min. per nozzle, and ha_H varied from about 0.35 to 2.7. The range of average water pressure on the nozzle was 3 to 15 lbs. per sq. in.

Coke-Packed Tower.—Whitman and Keats[1] give the following data for a tower packed with 3-in. gas coke and operated with a water velocity of 20 lb. per minute per square foot of total cross-section. Higher water velocities make little difference in the coefficient, but at lower velocities the coefficients drop off rapidly, probably due to incomplete wetting of the surface of the coke. These values of ha_H can be represented by the equation

Air Velocity. Pounds of dry air per minute per square foot of cross-section $= g$	Humidification ha_H	Dehumidification ha_D
8	4.55	1.60
11	5.85	2.60
14	7.05	3.70
17	8.40	4.90
20	9.65	6.30

$$ha_H = 1.20 + 0.42g$$

where g = air velocity as pounds of dry air per minute per square foot of total cross-section.

Slat-Packed Tower.—C. S. Robinson[2] gives the following:

For Water Cooling,

$$k'a_c = 0.0037u,$$

where u varied from 240 to 540 cu. ft. of air per min. per sq. ft. of ground area, $k'a_c$ varied from 0.50 to 2.18 lbs. water per min. per cu. ft. per unit $H_w - H$, and the water circulation was 53 lbs. per min. per sq. ft. of ground area.

Centrifugal Spray Tower.—Tests[3] on a Maclaurin scrubber gave the following results:

[1] *Loc. cit.*

[2] Recalculated from data given in *J. Ohio Soc. Mech., Elec. and Civil Eng.*, VII, 1.

[3] Littlefield, Merrill and Stewart, *M. I. T. Thesis*, 1921.

For Humidification,

$$ha_H = \frac{0.0823gL}{L+11},$$

where g varied from 3.5 to 15.3 lbs. dry air per min. per sq. ft. of total cross-section, ha_H varied from 0.12 to 1.10, and the water rate (L) varied from 3.4 to 117 lbs. per min. per sq. ft. of total cross-section. See Fig. 107.[1]

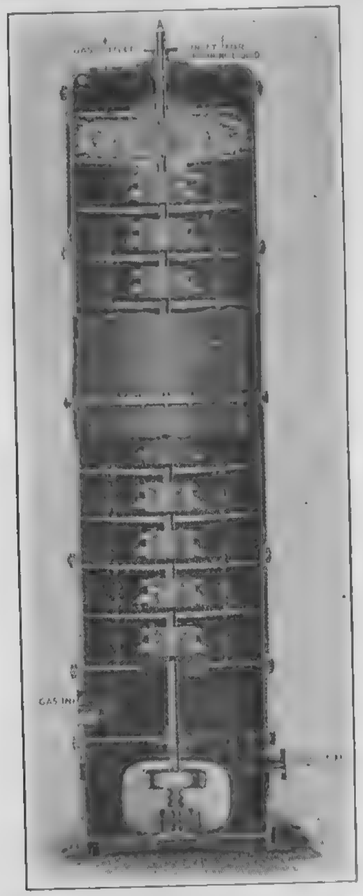


FIG 107.—Maclaurin Scrubber.

For $L=100$, $ha_H=0.0722g$.

For Dehumidification,

$$ha_D = \frac{g}{g+9.07},$$

where g varied from 2.8 to 13.0 lbs. dry air per min. per sq. ft. of total cross-section, ha_D varied from 0.18 to 0.60, and the water rate was 98 lbs. per min. per sq. ft. of total cross-section.

ILLUSTRATIVE PROBLEMS

In Problems (1) and (2), ha for a horizontal spray chamber may be taken as 1.50 for humidification and 0.50 for dehumidification, provided there are 12 lbs. of water per minute per spray, two sprays per sq. ft. of cross-section, and the banks are about 8 ft. apart (in the direction of flow of the air). The water pressure on nozzles may be taken as 20 lbs. gauge for new sprays when the rate of flow is 12 lbs. per min. per spray.

Problem 1. Humidifier.—It is desired to cool 22,000 cu. ft. per minute of air from 95 to 75° F., using a horizontal spray chamber which sprays the recirculated water against the air flow. The temperature of the make-up water is 80° F., the dew point of the initial air is 58° F., and the barometer is normal. Calculate:

(*a*) Number of spray nozzles required, and dimensions of chamber to house the sprays.

(*b*) Gals. of water recirculated per minute, and theoretical horsepower for spray nozzles.

(*c*) Gals. of make-up water per minute.

[1] *Courtesy of American Chemical and Sugar Machinery Co.*

Solution.—From Fig. 102, p. 448, it is seen that the humidity of air saturated at 58° F. is 0.0100, and that the per cent humidity of such air at 95° F. is about 28. Following the adiabatic cooling line, it is seen that the wet bulb temperature of this air is 70° F., and that the humidity attained during adiabatic cooling to 75° F. in contact with water is 0.0145, the per cent humidity being about 78.

The humid volume of air 28 per cent saturated at 95° F. is seen (by interpolation between the value of 14.82 cu. ft. for saturated air and 13.96 for dry air) to be 14.20 cu. ft. mixture per lb. of dry air. Then G equals

$$22{,}000/14.20 = 1{,}550 \text{ lbs. of dry air per minute.}$$

The sensible heat q removed by cooling the air, having initial humid heat of 0.2425, from 95 to 75 is, as seen by Eq. (1), (1550) (95−75) (0.2425), or 7520 B.t.u. per min. Since the *recirculated* water attains the wet bulb temperature (70° F.), the temperature difference between air and water is 95−70 or 25° F. at the entrance and 75−70 or 5° F. at the exit. From Eq. (2) it is seen that the *mean* temperature difference equals

$$(25-5)/(2.3)\ (0.699) \text{ or } 12.45° \text{ F.}$$

From Eq. (1) it is seen that

$$V = (q)/(ha)\ (t-T)_{av} \quad \text{or} \quad 7520/(1.5)\ (12.45) = 403 \text{ cu. ft.}$$

Since the value of ha used was determined for one nozzle per 4 cu. ft. and 2 nozzles per sq. ft. of cross-section, the theoretical number of nozzles equals 101, the sq. ft. of cross-section is about 51, and the length of spray chamber is about 8 ft. For 101 of these nozzles in one bank the water rate is

$$(101)\ (12)/8.33 \text{ or } 145 \text{ U. S. gals. per min.}$$

Since to evaporate one pound of water at 70° F. and warm the vapor to 75° F. one must supply 1065+0.48 (75−70) or 1068 B.t.u., the make-up water according to Eq. (3) equals 7520/1068 or about 7 lbs. of water per min., which is less than 1 gal. per min. It is obvious that the mixing of 7 lbs. of water at 80° with 1210 lbs. at 70° would not appreciably raise the temperature above 70° F. According to Eq. (4) the make-up water equals

$$(1550)\ (0.0145-0.0100) \text{ or about } 7 \text{ lbs. per min.}$$

The theoretical horsepower dissipated in the nozzles equals

$$(1210)\ (20)\ (144)/(62.3)\ (33{,}000) \text{ or } 1.7.$$

It can easily be shown that the dissipation of this power will not cause appreciable rise in water temperature. In calculating the actual horsepower of the motor for the pump, one must allow for the theoretical friction losses and lift in the piping system as well as the nozzle friction, and the combined efficiency of motor and pump. The calculated values are:

(*a*) 101 nozzles in one bank housed by a spray chamber 8 ft. long, and about 7 by 7.5 ft. in section.

(*b*) Water recirculated at rate of 145 gals. per min., the pump theoretically requiring 1.7 hp. for the resistance caused by the nozzles alone.

(*c*) About 1 gal. of make-up water required per min.

A safety factor should be included on the size of the spray chamber and number of nozzles to allow for decrease in effectiveness of sprays with time. The volume given above (403 cu. ft.) is that of the spray chamber alone; obviously, the actual apparatus must include air dampers at the entrance and water eliminators at the exit. Suitable strainers should be provided on the water line leading to the sprays. For use in winter heating coils should be provided. A typical calculation of the heating surface required is given on pp. 153 to 154.

Problem 2. Dehumidifier.—A horizontal counterflow spray chamber is to be designed to cool 5600 cu. ft. per min. of saturated air from 105 to 80° F., using cooling water entering at 45° F. Calculate:

(*a*) Number of spray nozzles required, and dimensions of spray chamber necessary to house them.

(*b*) Pounds of cooling water necessary per minute.

(*c*) Temperature of effluent water.

Solution.—In this problem there are primarily two unknowns: the number of nozzles (n) and the final temperature (T_1) of the water. Taking the arithmetic mean overall temperature difference, by Eq. (2*a*),

$$(t-T)_{av}=\frac{(105-T_1)+(80-45)}{2}=\frac{140-T_1}{2}.$$

By Eq. (1*a*), remembering that $V=4n$,

$$\frac{(5600)\ (105-80)\ (0.255)}{(15.4)}=\frac{(0.5)\ (4n)(140-T_1)}{(2)}.$$

Remembering that the rate of water supply (R) equals $12n$, the heat balance, Eq. (6) gives:

$$12n(T_1-45)=\frac{(5600)}{(15.4)}\ (105-80)\ (0.255)+\frac{(5600)}{(15.4)}\ (0.0497-0.022)\ (1050).^{1}$$

Solving these two equations gives:

$$T_1=75°\text{ F.}$$
$$n=36.$$

Whence, V equals 144 cu. ft., *i.e.*, 8 ft. long by 4 ft. by 4.5 ft., and R equals 432 lbs. of water entering per min., or 51.8 gals. per min. See notes in preceding illustration concerning safety factor.

Illustration 3. Water Cooler.—A slat-packed cooling tower is to be designed to cool 3000 gals. per min. of condenser water from 110 to 85° F.

[1] To be more exact, this value of r at the average air temperature should be corrected for the cooling (or heating) of the condensate from this average temperature to the temperature of the exit water.

by means of air flowing up through the tower. With forced draft, it is estimated that the velocity of the entering air will be 500 cu. ft. per min. per sq. ft. Under the worst conditions the available air will be saturated at 80° F.

Using the data given below, and neglecting heat losses to the surroundings, calculate:

(*a*) Cu. ft. per min. of air entering the tower.

(*b*) Height and ground area of tower.

(*c*) Temperature and humidity *of* exit air.

Data.[1].—For similar towers handling 53 lbs. of water per min. per sq. ft. ground area, it is found that $k'a=0.0525g$, where g equals lbs. of dry air per minute per sq. ft. of total cross-section, $k'a$ for Eq. (7) being expressed as lbs. of water evaporated per min. per cu. ft. of *total* volume per unit (H_w-H), where H_w equals the humidity as lbs. of water vapor per lb. of dry air at the water face of the air film on the water surface, and H is the humidity of the air flowing past the water surface. For this type of tower used as a water cooler, $ha/k'a=0.33$.

Solution.—Since the data available for ha and $k'a$ were determined for 53 lbs. water per min. per sq. ft. of total cross-section, the ground area of the tower equals (3000) (8.33)/53 = 472 sq. ft. The volumetric capacity of the fan equals (472) (500) = 236,000 cu. ft. per min. at 80° F. Since the humid volume of the entering air is 14.1 cu. ft. per lb. of dry air, G equals

$$(472)\ (500)/(14.1)=16{,}700\text{ lbs. dry air per min.}$$

(It will be noted this corresponds to about two-thirds lbs. of dry air per lb. of water fed.)

The heat balance for the tower, Eq. (6*a*), is:

$$(16{,}700)(s_{av})(t_2-80)+(16{,}700)(H_2-0.0220)(1046)=25{,}000(110-85). \quad . \quad (A)$$

The equation for the transfer of sensible heat to the air, Eq. (1*a*) is:

$$(16{,}700)(s_{av})\ (t_2-80)=haV\left(\frac{110-t_2+85-80}{2}\right).$$

Since the velocity (g) of dry air is 16,700/472 = 35.4 lbs. dry air per min. per sq. ft. of total cross-section, $k'a$ equals 0.0525 (35.4) = 1.86, and ha = (0.33) (1.86) = 0.614.

Hence the preceding equation becomes:

$$(16{,}700)\ (s_{av})(t_2-80)=(0.307)(V)(115-t_2). \quad . \quad . \quad . \quad . \quad (B)$$

The equation for the diffusion of water vapor into the air, Eq. (7) is:

$$(16{,}700)(H_2-0.0220)=(1.86)(V)\left(\frac{0.0584-H_2+0.0260-0.0220}{2}\right),$$

or

$$16{,}700(H_2-0.0220)=(0.93)(V)(0.0624-H_2). \quad . \quad . \quad . \quad (C)$$

[1] ROBINSON, *loc. cit.*

Since,

$$s_{av}=0.238+0.48\left(\frac{0.022+H_2}{2}\right),^{*}$$

there are three equations (A, B and C) and three unknowns: V, H_2 and t_2. If Eq. (B) is divided by Eq. (C), V is eliminated, and hence values of t_2 and H_2 must satisfy (A) and (B/C). As a first trial, t_2 is usually taken as 5° F. less than the temperature of the entering water. The values of t_2 and H_2 which satisfy the above conditions are:

$t_2=107°$ F.

$H_2=0.0512$ or 96.5 per cent saturated.

Substituting these values in Eq. (C), and later in (B) as a check of the arithmetic, $V=47{,}000$ cu. ft. Hence the height of the tower equals

$$(47{,}000)/(472)=99.5 \text{ ft.}$$

NOTE.—This cooling tower was designed for the "worst conditions" of the air, namely, *saturated at 80° F.* When the air is not saturated, or cooler than 80° F. or both, the water will be cooled to a temperature lower than 85° F. Since the calculated height of 99.5 ft. is excessive, the designer would probably compromise by using a shorter tower, thereby sacrificing somewhat the cooling of the water.

DERIVATION OF EQUATIONS

Equations for Adiabatic Humidification.—The simplest technical application of the evaporation of water into air is in humidifiers. Only a small fraction of the water fed in as spray is taken up by the air, but as the excess water is collected and recirculated, only the evaporation being made up by a fresh supply, the water temperature is that of the wet bulb throughout the process. Even in those cases where entirely fresh water is used, the wet bulb temperature is soon reached unless the supply be unusually hot or cold. Consider such a chamber of length L (feet), and cross-section A (sq. ft.), into which G lbs. of bone-dry air of humid heat s enter per minute, and in which is produced a spray of such character that the total surface area (sq. ft.) of all the drops contained per unit volume (cu. ft.) of the chamber is a. Consider any section at right angles to the direction of flow of the air of thickness dL. The volume of this section is $A\,dL$ and the area of the drops contained therein is $A\,a\,dL$. If the temperature of the air at this point be t (° F.) and of the water T_w (° F.) the quantity of sensible heat transferred from the air into the water per unit time is expressed by Newton's law:

$$dq=(h)\ (aAdL)\ (t-T_w). \quad \ldots\ldots\ (a)$$

* The use of this equation complicates the solution of the problem, and since s varies only slightly, it is advisable to assume it as constant.

Since this heat comes from the cooling of the air,

$$dq=-Gsdt. \quad \ldots\ldots\ (b)$$

Equating the sensible heat removed from the air to that transferred to the water gives

$$\frac{dt}{(t-T_w)}=-\frac{haA\,dL}{Gs}. \quad \ldots\ldots\ (c)$$

In such a system, under definite operating conditions, each factor in the coefficient of dL will remain constant, and for convenience may be written,

$$\frac{haA}{Gs}=c, \quad \ldots\ldots\ (d)$$

or

$$\frac{dt}{(t-T_w)}=-cdL. \quad \ldots\ldots\ (e)$$

Inasmuch as the wet bulb temperature, T_w, is constant throughout the chamber, it is possible to integrate directly between the limits of t_1 and t_2, O and L giving

$$ln_e\left[\frac{t_2-T_w}{t_1-T_w}\right]=-cL, \quad \ldots\ldots\ (f)$$

where t_1 and t_2 denote the temperatures of the air at the inlet and exit of the apparatus respectively, and L the total length of the spray chamber. This last equation may be re-written

$$\frac{(t_2-T_w)}{(t_1-T_w)}=e^{-cL}. \quad \ldots\ldots\ (g)$$

If both sides of the equation be subtracted from unity, giving,

$$\frac{(t_1-t_2)}{(t_1-T_w)}=1-e^{-cL}, \quad \ldots\ldots\ (h)$$

it is seen that the cooling secured in an actual apparatus, divided by that possible for the same air in a perfect humidifier, is a constant for the given apparatus and conditions. Since a perfect chamber would produce absolutely saturated air, this last expression is called the fractional humidification of the given installation, or more frequently, when multiplied by 100, the per cent humidification.

Combining Eqs. (d) and (f), one obtains:

$$ln_e\left[\frac{t_1-T_w}{t_2-T_w}\right]=\frac{haV}{Gs}, \quad \ldots\ldots\ (i)$$

where V is the total volume of the system.

If one writes

$$q = Gs\,(t_1 - t_2) = haV\,(t - T_w)_{av}, \quad . \quad . \quad . \quad . \quad (j)$$

by analogy to the integrated form of Newton's law for heat transfer, where

$$(t - T_w)_{av} = \frac{(t_1 - T_w) - (t_2 - T_w)}{ln.\dfrac{t_1 - T_w}{t_2 - T_w}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (k)$$

it is seen that a combination of Eqs. (*j*) and (*k*) give Eq. (*i*) which was derived from the calculus for humidification. This confirms the statement in the text that Eq. (5) is merely another form of Eq. (1), and justifies the use of the logarithmic mean temperature difference.

CHAPTER XVI

DRYING

PART ONE: METHODS OF DRYING

Introduction.—Although the term drying may have a peculiar significance in a few specialized industries, in general engineering practice it may be taken to mean the removal of water from a system or structure, when the amount of water present is comparatively small. For purposes of study the subject matter may be classified from a number of different points of view.

The material to be dried may be either a gas, a liquid, or a solid. If a gas, the water may be carried simply as vapor, or in addition it may be present in the form of a spray or fog. If a liquid, water is removed by *drying* only when present in small amounts; otherwise the process is described as evaporation or distillation. Thus fusel oil, alcohol or acetone may be "dried" by removing the water therefrom. In solids the amount of water may vary from a mere trace to the large amount present in fresh fruit or in a glue jelly.

As the moisture leaves a wet solid there is often a tendency for the structure to diminish in volume, or shrink. If great care be not taken this shrinkage will not be uniform, and cracking or warping results, which deteriorates the product. Examples of this action are found in timber and unburned pottery. Or, if a material be dried under tension and lateral shrinkage prevented, the structure loses its strength. Such is the case when paper is dried on certain machines as compared to that slowly dried in a loft. Many materials such as eggs, fruit, or milk must be dried rapidly at as low a temperature as is practical, in order to preserve their characteristic flavor and the other valuable properties they possess. Some substances deteriorate when allowed to remain for a considerable length of time in a wet condition. Material, such as glue, starch, and sugar, cannot be heated while

wet owing to the solvent action of the water upon them. Many substances containing water of crystallization cannot be dried under ordinary conditions because of a loss of all or a portion of this water. These widely varying conditions may be cared for in drier design by considering the rate of drying, condition of the drying medium, and the nature of the exposed surface. Each of these factors is complex, and will be discussed in detail later.

Methods of Drying.—The available methods of drying are:

1. Deposition of the moisture either as water or ice.
2. Decomposition of the water.
3. Chemical precipitation.
4. Absorption.
5. Adsorption.
6. Mechanical Separation.
7. Vaporization.

The completeness with which dryness can be effected by any process depends upon the factors controlling the equilibrium conditions then obtaining. These will be considered as each method is discussed.

1. Deposition of the Moisture as Water or Ice.—When condensation takes place in a gas it is obviously the reverse of vaporization and depends upon the same fundamental considerations. The clumsy term dehumidification has come into general use for operations of this character and the subject has been treated together with humidification processes. The Gayley dry blast for smelting iron is an example of the large scale application of this idea.

Water may be removed from liquids by converting it into ice and in this form separating it from the portion having a lower freezing point. The alcoholic content of a liquid possessing a delicate flavor can in this way be readily increased. Fruit juices are concentrated by cooling with agitation, and subsequently separating the ice crystals by passage through a centrifugal machine.

The amount of moisture remaining in air dried by cooling depends upon the temperature to which it is cooled. Also in the case of a liquid it depends upon the temperature reached, but is limited when an eutectic mixture is formed.

2. Decomposition of the Water.—When a small amount of water is held in either a gas or a liquid, it may be removed by

decomposing it and separating the products formed. Thus ether is dried by placing it in contact with metallic sodium. The caustic soda formed clings to the surface of the metal and if separated will eventually settle out. Certain circumstances allow of using other water-decomposing agents such as the carbides, and nitrides. Here the completeness of the process is largely a function of mechanical agitation of the liquid and the reacting substance. The vapor pressure of water with which the substances formed are in equilibrium is so small as to be negligible.

3. Chemical Precipitation.—Somewhat larger amounts of water may be advantageously withdrawn in the form of a chemically combined precipitate. Thus lime forms calcium hydroxide; anhydrous sulphate of copper or sodium takes on water of crystallization and separates from the liquid. The amount of water remaining in the liquid is controlled by the vapor pressure of the hydroxide, or the crystalline substance formed. Phosphorus pentoxide and calcium chloride may be used for drying gases, and for liquids in which they are insoluble; again the completeness of drying is limited by the vapor pressure of the resulting hydrated substance.

4. Absorption.—In some technical processes water is removed from a material by the capillary action of porous bodies. Thus the cream of clay and water used for casting pottery is deprived of the greater part of its water by placing it in molds of plaster of paris. The capillary character of this mold withdraws the water from the liquid clay mixture and deposits upon itself a layer of solid clay, the thickness of which is controlled by the time of standing. Certain types of candies, such as gumdrops, are dried mainly due to contact with the starch molds in which they are cast. The drying effect of sponges, towels, and materials of this kind is due to this same action.

5. Adsorption.—The wonderful ability of certain substances to adsorb moisture makes possible the application of this process for drying gases, and to some extent also liquids. See pages 630 to 721.

6. Mechanical Separation.—Some materials are of a spongy nature and hold by capillarity large quantities of moisture which may be expelled by pressure alone. When such is the case it is evidently desirable to so get rid of as large a percentage as possible before passing to other more expensive methods. This may be

readily accomplished in many cases (textiles, wool, grain and the like) by centrifugal force. (See p. 354.) Or a positive pressure may be exerted by a screw as is shown in Fig. 108.*

7. Vaporization.—By far the most important processes for drying liquids and solids depend upon first vaporizing the water and in this form separating it from the structure of which it formed a part. If air or some inert gas be used to carry away the water vapor formed, the process is called Air Drying. If the vapor be passed to a condenser, a pump being employed to withdraw the air from the apparatus, the process is spoken of as

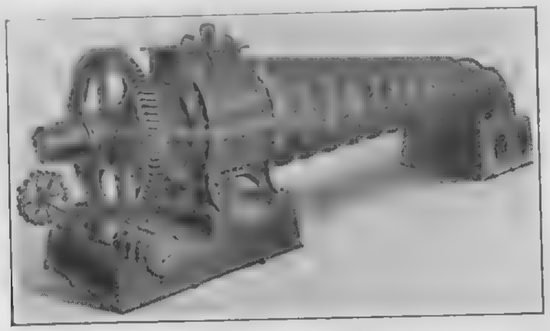


FIG. 108.—Screw Press.

Vacuum Drying. By far the greater proportion of this chapter is devoted to drying by means of vaporization.

PART TWO: GENERAL PRINCIPLES OF DRYING BY VAPORIZATION INTO A GAS

General Considerations.—Every solid and liquid substance exerts at any definite temperature a perfectly definite vapor pressure. If the substance be a mixture, each component exerts its own particular and definite vapor pressure. These separate or partial pressures are additive and together make up the total vapor pressure of the substance. If the component parts of a mixture are mutually soluble the partial pressure of each component will be thereby somewhat decreased. The vapor pressure of liquids increases as the temperature rises and obviously there will be some definite temperature at which this vapor pressure equals the pressure of the atmosphere. At this point the vapor of the liquid will continue to form, and not only diffuse but actually push back the atmosphere into space, maintaining as total

* *Courtesy of American Process Co.*

pressure the atmospheric pressure then existing. The liquid is then said to boil and this temperature is called its boiling point. As the pressure of the atmosphere varies, clearly the boiling point of a liquid will vary also.

These elementary conceptions are so essential to a ready understanding of the discussion which follows that the reader is referred to pages 380 to 387, for further exposition of them.

As the science of drying developed, there were adopted a number of expressions which at times vary in their meaning from that which normally attaches to them. A full discussion of these definitions is given in the chapter entitled Humidity and Wet and Dry Bulb Thermometry. (See pp. 441 to 443.)

MECHANISM OF AIR DRYING OF SOLID MATERIALS

The discussion of the Mechanism of Vaporization of Liquids Suspended in Air (pp. 443 to 444) has shown the influence of the temperature and humidity of the air with which pure water is in contact upon its rate of vaporization; it will develop later that the velocity of the air past the water surface is also a factor of importance. It will now be shown that, when water is admixed with other materials, the composition and form of the mixture profoundly modify the evaporative rate. In order to determine the effect of changing value of these new variables, they will first be studied under constant drying conditions.

Most solid materials to be dried exist in either sheet or lump form with the water[1] from which they are to be freed disseminated throughout the mass. The mechanism of removal of this water is somewhat complicated, but must be thoroughly understood in order to appreciate the factors controlling the drying of such materials.

For the sake of definiteness consider the drying of a sheet material freely and equally exposed to the drying air on both sides of the sheet. The sheet will be assumed so large in comparison to its thickness that the drying from the edge of the sheet may be neglected, as compared to the drying from the faces of the sheet. It will be assumed that, initially, the water is uniformly distributed throughout the thickness of the sheet. As soon as

[1] Although water is the liquid used in this discussion, it should be remembered that a similar treatment applies to other liquids.

the sheet comes into contact with the drying air, evaporation will start at the surface, and the concentration of water on the surface will therefore diminish. This will cause a difference in concentration between the interior of the sheet, which is still wet, and the surface, which has been partially dried by evaporation. In consequence of this concentration difference, there will be a flow of liquid water *by diffusion* from the interior of the sheet to the surface, to replace that lost *by evaporation* from the surface. These two processes, *i.e.*, evaporation from the surface, and diffusion through the sheet from the interior to the surface, will go on simultaneously until the drying operation is suspended, or the sheet has come into equilibrium with the drying air. In some cases, surface evaporation is the controlling factor in drying, while in others the resistance to diffusion of the water from the interior to the surface limits the rate of drying. In any case, it is essential to keep in mind the part played by each of these processes in order intelligently to control the drying operation.

Diffusion of Liquid Limiting Factor.—The importance of these two processes will be appreciated from the following illustrations. Wet, green wood must be dried prior to use. During the drying it shrinks. If the surface evaporation be excessively rapid, the surface becomes very dry while the interior is still impregnated with moisture, *i.e.*, there is set up a large gradient in moisture concentration from the interior toward the surface. The surface shrinks owing to the evaporation of its moisture, and is put under high tension because of the incompressible character of the wet interior. If the surface shrinkage is excessive, this results in rupture of the surface with the production of cracks or checks which ruin the lumber for finer uses. In drying such lumber it is therefore essential to avoid setting up too large a concentration gradient between the surface and the interior, and this is done by employing the highest safe rate of diffusion and making the rate of surface evaporation commensurate to the rate of diffusion of water.[1] Exactly the same applies to the drying of articles molded from wet clay in the ceramic industry.

Surface Evaporation as Limiting Factor.—In the drying of paper, chrome leather, and similar materials, the sheets possess

[1] For the method of securing rapid drying without creating an excessive gradient through the stock, and hence without producing checking, see p. 493.

a finely fibrous structure which distributes the moisture through them by capillary action, thus securing very rapid diffusion of moisture from one point of the sheet to another. This means that it is almost impossible to remove moisture from the surface of the sheet without having it immediately replaced by capillary diffusion from the centre. The drying of such sheets is, therefore, essentially a phenomenon of surface evaporation.

Mechanism of Surface Evaporation.—In any case, the phenomenon of surface evaporation is a diffusion of water vapor from the surface of the sheet through a relatively stationary air film in contact with that surface to the surrounding air, into which further dissemination is rapidly effected by convection. As emphasized elsewhere[1] a solid in contact with a gas has on its surface a relatively stationary film of that gas which serves as an insulating layer between the gas and the solid. This film is relatively thick when the motion of the gas is slight, but with high velocity of the gas past the solid surface the thickness of this film rapidly decreases, the film never, however, disappearing. In the case of the evaporation of water from a wetted, solid surface into air, the inner layer of the air film in contact with the solid is maintained saturated with moisture as long as the moisture content of the sheet is sufficient. If the outer air surrounding the body is unsaturated, this means that there is a partial pressure gradient of water vapor from the surface of the sheet out through the stationary film to the outer air; and owing to this gradient, water vapor diffuses from the sheet outward. Vapor reaching the outside of the air film is disseminated by convection throughout the mass of the surrounding air at a rate so great, in comparison with the rate of diffusion through the stationary air film, that concentration differences of water vapor in the surrounding air may be neglected.

Factors Controlling Surface Evaporation.—According to Newton's law of diffusion, the rate of diffusion (weight per unit of time) of any gas varies *directly* as the cross-sectional area of path (taken at right angles to the direction in which the gas is diffusing), *directly* as the difference of pressure of the gas at the two points in question, and *inversely* as the length of path. The rate of diffusion of water vapor from the surface of such a sheet out through the air film on its surface will therefore be

[1] See pp. 36 to 42.

(*a*) directly proportional to the exposed area of the sheet,

(*b*) inversely proportional to the thickness of air film, and

(*c*) directly proportional to the difference in pressure between water at the temperature of the inner film surface and the partial pressure of water vapor in the surrounding air. As pointed out elsewhere (p. 443), the sheet tends, as long as it remains sufficiently wet, to assume the wet bulb temperature of the air in which it exists, so that, for given conditions of the drying air, the driving force causing diffusion, Δp, is known. The thickness of the air film, *i.e.*, the distance through which diffusion must take place, is not known; it is, however, a function of velocity, decreasing with increasing velocity; the diffusion, therefore, increases as the velocity goes up.

Inasmuch as the evaporation of water is accompanied by a definite and large absorption of heat, this heat supply must be maintained in order that evaporation may proceed. This heat supply must, in general come from the surrounding air by conduction[1] through the air film, and is proportional to the temperature difference. Since this heat supply exactly compensates for the evaporation, the temperature difference between the air and sheet must be proportional to the pressure difference of water vapor between the sheet and air. This is merely a reiteration of the principle developed in the discussion of wet and dry bulb thermometers.

Effect of Vapor Pressure Lowering.—Since the rate of drying is proportional to the difference between the vapor pressure of the liquid and its partial pressure in the surrounding space, it follows that material which is appreciably soluble in the liquid with a consequent vapor pressure lowering in the liquid, will dry more slowly than one which is insoluble. Thus sand carrying a definite weight of water will dry more rapidly than common salt of the same water content, other things being equal.

Effect of Adsorption.—It is well known that certain materials contain definite, and sometimes appreciable, percentages of moisture when exposed indefinitely to air of a given temperature and humidity. This water is probably adsorbed; in any event

[1] This is not the case where radiant heat is employed, or where the stock is in direct contact with the heating surface. However, the above discussion deals with *air* drying.

it represents a true dynamic equilibrium Fig. 109[1] shows the per cent equilibrium moisture of textiles plotted against the per cent *relative* humidity of air at various temperatures. For all materials investigated[2] the shapes of the curves are similar to those shown in Fig. 109 and the per cent equilibrium moisture for a given per cent relative humidity always decreases as the temperature rises. However, raising the temperature produces only a slight decrease in the per cent equilibrium moisture, and hence interpolation between curves at two temperatures is satisfactory. At the per cent relative humidities ordinarily encountered the

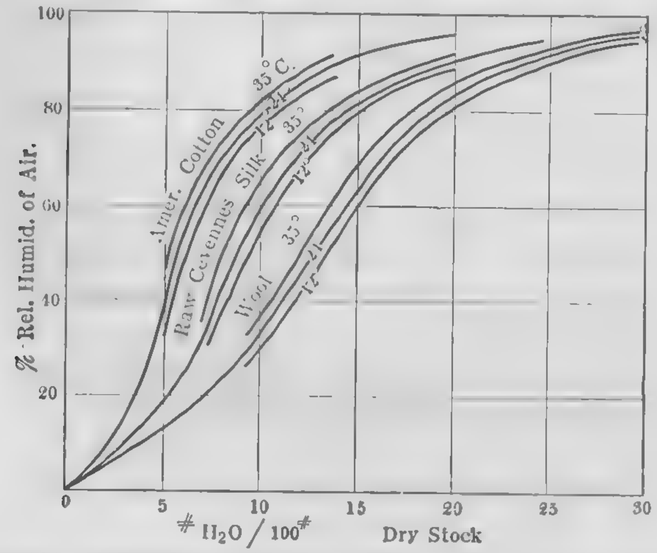


FIG. 109.—Humidity-moisture Equilibrium Curves for Textiles.

percentage of adsorbed water is appreciable in the case of certain amorphous organic substances, such as cotton, silk, wool, leather, paper, flour, and the like. Only the moisture in excess of that adsorbed, namely the total minus the equilibrium moisture, is subject to removal. For more complete drying, high temperatures or very dry air is necessary.

PART THREE: DRYING APPARATUS AND AUXILIARY EQUIPMENT

The two fundamental factors controlling the rate and completeness of drying, namely the supply of heat and the removal

[1] Data from M. T. SCHLOESING, JR., *Bull. soc. encour. ind. nat.*, **1893**.

[2] R. E. WILSON AND T. FUWA, *J. Ind. Eng. Chem.*, **14**, 913 (Oct., 1922).

of the vapor formed, have been presented[1] as a basis for drier design and operation, but without regard to the mechanical means for making these factors effective. Unless the source of heat be the sun, and the removal agency be the natural air currents, it is clear that an enclosing structure must be provided, and that the material to be dried must be moved into and out of this structure. A discussion of the driers now commercially available will therefore be presented, first from the point of view of the method of moving the material and air in the drying enclosure, and second,[2] the method of supplying heat for the drying operation.

Intermittent vs. Continuous Driers.—In most forms of driers, the operation can be either intermittent or continuous, that is, the charge may be placed in the enclosure and allowed to remain there until dried, then removed and its place taken by a fresh charge; or, the charge may pass through the enclosure, entering one end wet and coming out the other end dry.

The advantages attaching to an intermittent drier are economy in construction, simplicity in operation, and opportunity for variation of the drying conditions. It is easy to build and inexpensive to maintain, and for experimental work or small installations it has these points to recommend it. On the other hand, in almost every industry, continuity of operation offers marked advantages in routing material in process through the plant, and in lower labor costs in transporting and working the same. But in air drying, continuous operation has two additional advantages so great that intermittent drying is justified only when the amount to be handled is small, or the most exact control of the drying conditions is required.

In the first place the heat economy of an intermittent drier is very poor. While the thermal efficiency at the beginning of the operation is high, the hot dry gases quickly taking up a large amount of water from the wet stock, the rate of evaporation rapidly decreases as the water content of the stock falls. The result is that the heat content of the circulating air is utilized to a small and decreasing extent as the drying proceeds. Second, an intermittent drier is irregular in its action, producing as a rule non-uniform product. The material in immediate contact with the hot dry air as it enters loses its moisture more rapidly than

[1] See pp. 386 to 387.

[2] See pp. 509 to 510.

that in contact with the cooler and more humid air leaving the apparatus. This results in either removing the product while a portion is but partly dry, or in reducing the capacity of the drier by retaining a part of the material after it is completely dry. In any case continual attention on the part of the man in charge is demanded, necessitating an operator of the grade and with the wage scale of an inspector. Even then a continual error of judgment is introduced, which, with continuous operation and automatic control, is eliminated.

It is none the less possible by the use of an intermittent drier to secure more exact control of the drying conditions throughout the drying schedule than in any other way. On this account such a drier is recommended for those cases in which the drying rate must be continuously varied throughout the drying period, as in drying lumber, to prevent, "case hardening" and the resulting evils of cracking, warping and the like. (See pp. 493 to 495.)

DESCRIPTIVE CLASSIFICATION OF DRIERS

For the purpose of discussing the method of moving the material to be dried and the air for drying, the following classification of driers is made:

- A. Intermittent Driers
  - Loft
  - Compartment
  - Chamber
  - Cabinet
- B. Continuous Driers
  - Tunnel.....
    - Parallel Current
    - Counter Current
  - Drum.....
    - Atmospheric Pressure
    - Vacuum
  - Rotary.....
    - Parallel Current
    - Counter Current
    - Reversed Current [1]
    - Vacuum
  - Spray Driers
    - Atm. Press.
      - Hot Air
      - Superheated Steam
    - Vacuum

[1] A combination of parallel and counter-flow.

A. Intermittent Driers

Since the rate of drying is proportional to the area exposed per unit of weight, it is advantageous to so dispose the material that all sides will be effective in evaporation. This is usually accomplished by hanging sheet material from hooks or bars and by supporting lump or granular material upon perforated trays or shelves. These trays may be either placed on supports in the drying chamber, or held in a framework on a truck which can be run into the chamber. The latter method has the advantage of being easier to load and unload, the entire truck being mechanically turned on its side for the latter operation. Frequently transportation through the plant may be effected while the material is loaded for the drying operation.

Loft Driers.—The simplest form of drying chamber is a room or "loft" containing steam coils arranged in various ways within it. Such have been used in the past for drying writing paper, leather, fibre board and products of this type. These driers are bad from many standpoints. First, it is impossible to secure uniform distribution of heated air if the loft be of any size. There will always be air pockets and channels where the velocity will be either negligible or excessive. This makes uniformity of product impossible unless all the material is allowed to remain until the slowest drying is finished, greatly cutting down the capacity of the drier. If that which is dry be removed and a fresh charge introduced, the drying of that nearly complete will be interfered with by the excessive moisture content of the air passing over the wet stock. The labor cost of constant inspection and the floor space required are factors not to be overlooked.

Cabinet, Compartment and Chamber Driers.—However, where a material must be dried very slowly to produce the best results, as in fine writing paper and heavy sole leather, a drier of this type produces a high grade of product. The above disadvantages may be overcome at a low cost by building the drier in small compartments or chambers arranged around a central exhaust, and causing the air to be circulated in accordance with the principle of the ring furnace. (See p. 230.) This will secure practical continuity of operation, excellent distribution of the heat and drying air, and a lower labor cost.

When the material is lumpy or granular, or if it cannot be supported by hooks or bars, trays or racks are employed and these placed as a rule in a smaller space usually spoken of as a cabinet or compartment. For small self-contained installations chamber driers as shown in Fig. 110 are very satisfactory, and can be readily installed and operated. However, their overall efficiency is poor compared to a continuous drier.

Lumber must be dried in accordance with a definite time schedule, the temperature being the maximum and the humidity the minimum that the stock will bear without injury, to secure rapid diffusion with a limited concentration gradient through the stock. The drying conditions vary with the species and with the

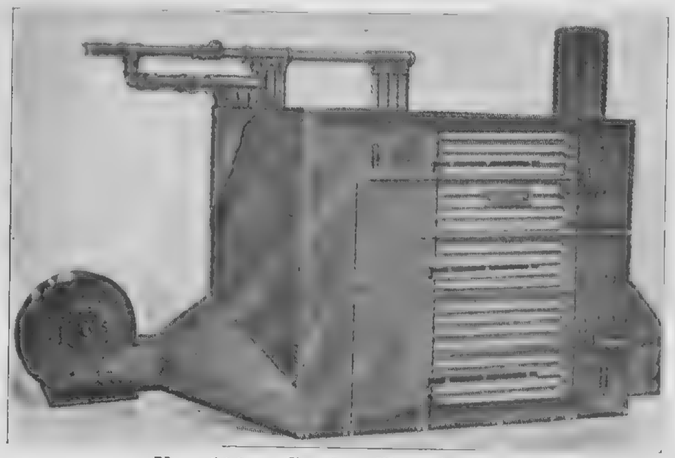


Fig. 110.—Gordon Tray Drier.

thickness of the stock, a characteristic schedule being given in Fig. 111.[1] The air temperature is marked T, the dew point D, and the per cent relative humidity H.

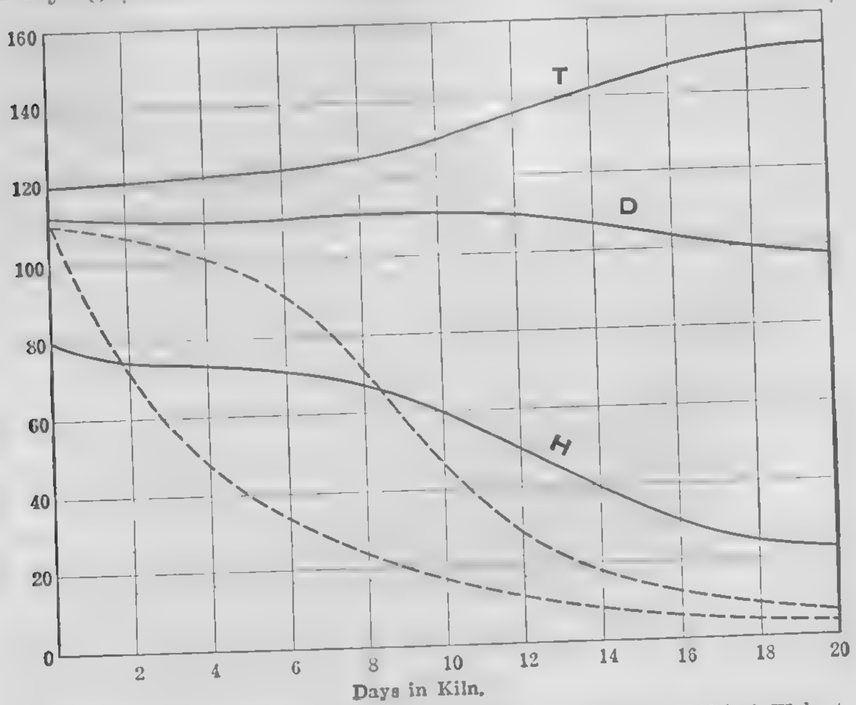
The maintenance of this schedule is most easily effected by intermittent operation of the chamber or kiln employed. A modern type of kiln is shown in Fig. 111A.[2] The kiln is enclosed and the drying air recirculated by natural convection, the lumber being slanted to utilize the increase in density of the air with evaporation to facilitate the movement. The air leaving the pile is partially dehumidified by the water spray F and then

[1] H. D. Tiemann, "The Kiln Drying of Lumber," J. B. Lippincott Co., Phila., 1917.

[2] Tiemann, *loc. cit.*

reheated by the steam pipes *H*. The drying conditions are controlled by two thermometers inserted below and above the steam coils, the former showing the dew point and the latter the dry bulb temperature of the drying air.

The two dotted curves in Fig. 111 show the moisture content of the wood at the points where the air enters the pile and leaves it. The horizontal distance between these two curves is the "lag" in drying caused by the increase in the moisture content of the



Drying Conditions Suitable for One Inch Red Gum, Black Gum and Black Walnut

FIG. 111.—Drying Schedule for Wood.

air as it passes through the pile. This emphasizes the inadequacy of natural circulation in such a case. Higher air velocity, or periodical reversal of its direction of flow, would dry the whole pile at the fastest rate allowable.

Attention is called to the care exercised in the design of this kiln to prevent air circulation other than through the pile and to secure uniform distribution of the air through the stock.

Drying in Vacuum.—In the driers so far described, air is used to carry away the water vapor from the drying material. When the nature of the product is such that it cannot be maintained

hot in contact with air, or when drying at a low temperature is imperative, or when it is desired to condense and recover the liquid volatilized, vacuum driers are employed. These are either shelf or drum driers enclosed in an air-tight vessel strong enough to sustain an external pressure of 15 lbs. per sq. in., or a rotary drier in which may be maintained a diminished pressure. The air and any fixed gases entering with the material to be dried

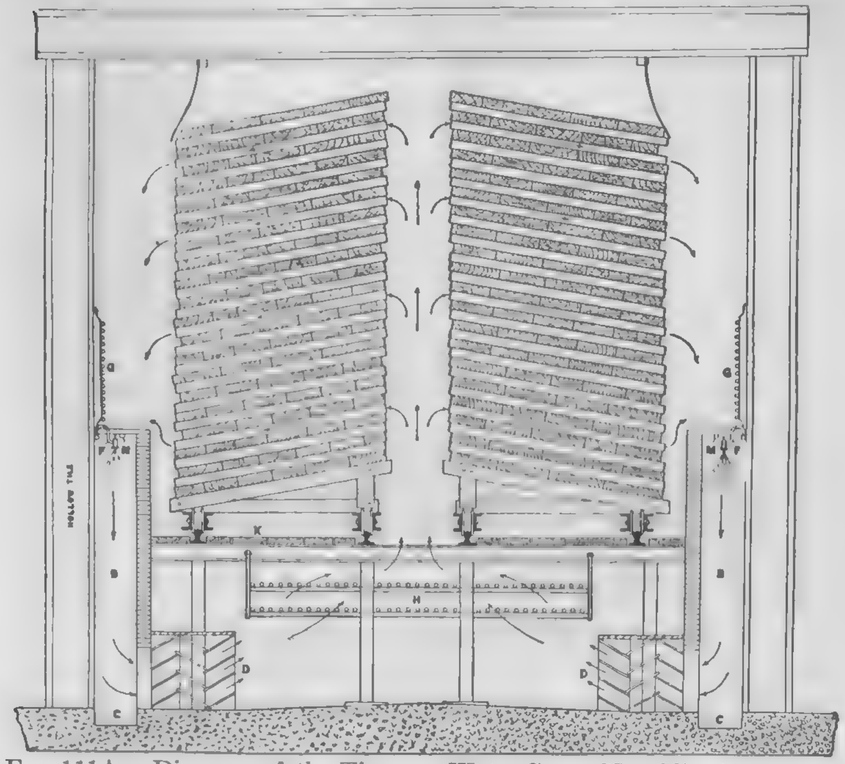


FIG. 111A.—Diagram of the Tiemann Water Spray Humidity Regulated Dry Kiln. (Cross-sectional elevation.)

are exhausted by a pump, and the vapor formed is led to a suitable condenser. Direct-heated shelf driers are of simple construction, the heat being introduced by means of steam coils and plates on which the trays are supported. They cannot easily be made continuous.

B. Continuous Driers

Tunnel Driers.—It is evident that if the hooks, bars, or trays, on which the material is supported be moved through

the drying space that the operation becomes continuous. The space will then be made long in relation to its cross-section and the apparatus is spoken of as a tunnel drier (Fig. 112[1]). Instead of moving the stock by supports placed on trucks, it may be propelled on an endless belt or moving platform, or other type of traveling conveyor (Fig. 113).

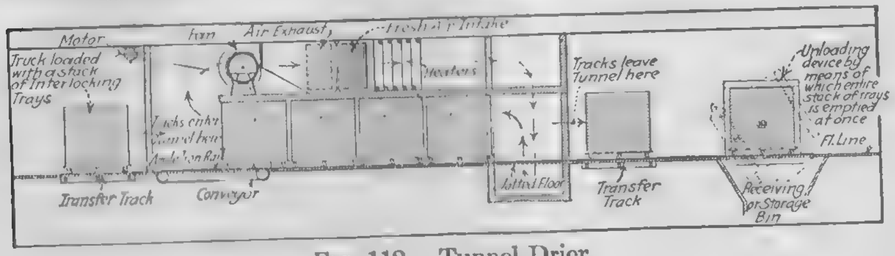


FIG. 112.—Tunnel Drier.

The heated drying air may be made to pass in the same direction as the stock, *parallel flow*, or it may pass in a direction opposite to that of the stock, *counter-current flow*. It is obvious that for efficient use of the heat and moisture-carrying capacity of the air the counter-current method is in every way superior and should be used. When, however, it becomes necessary to have the stock leave the drier with a definite amount of moisture, or when so-called "case hardening" of the material is liable to

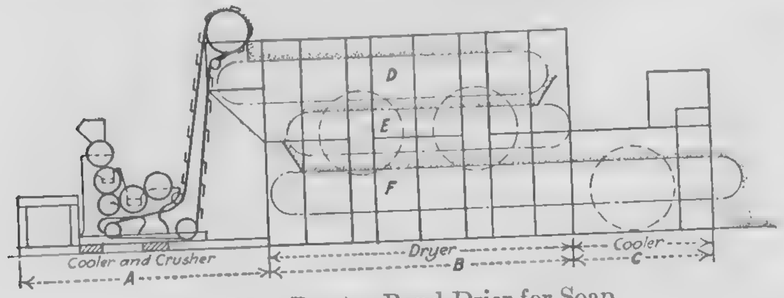


FIG. 113.—Proctor Band Drier for Soap.

occur, parallel flow gives a more satisfactory control of the temperature and humidity obtaining throughout the operation. Whenever allowable heating elements (usually steam pipes) should be distributed through the space so as to keep the air at such a temperature that a satisfactory rate of evaporation may be obtained without overheating the product or causing undue

[1] *Courtesy of Drying Systems, Inc.*

loss of heat in the discharged material. Tunnel driers are increasing in popularity as they are not expensive to construct and are satisfactory in operation and product.

Drum Driers for Solids.—When the material to be dried is in the form of a continuous web, as for example paper or cloth, it is generally dried by passing it over steam-heated cylinders or drums,—either by itself or held to the drum by an endless felt. The temperature of the sheet may be maintained near the boiling point of water and since in passing over successive drums it is heated on alternate sides very rapid evaporation is effected. In order to increase the capacity of such a system, sometimes a blast of warm air is directed on the stock. In a series of drums of the same diameter running at uniform speed, the linear velocity at a point near the wet end is the same as one at the dry end. If the material tends to shrink in drying, it must evidently suffer mechanical elongation of the sheet equal to the natural contraction of the material. Thus paper dried on a rapidly driven continuous machine has less tensile strength than the same stock dried slowly in a loft where it is free to shrink as the water leaves it. Apparently the difficulty could be met by rotating succeeding drums at a decreased rate of speed, or in making the drums with a successively smaller diameter.

Drum Driers for Liquids.—Many finely divided materials are of such character that when supplied in the form of a thick cream or mush they cling to the surface of a heated drum (Fig. 114) and are dried while the drum makes one revolution. Since the surface of the drum is the only source of heat it is clear that it should be maintained at as high a temperature as the material being dried will tolerate. The thickness of the layer of material is regulated by a scraping knife or "doctor" on the feed side, and the dry product is removed from the surface of the drum by a similar mechanism.

For a very large output of material the surface may be horizontal and the drier takes the form of rotating disk or plate on which the material is fed through a slit from above. The discharge is effected by scraping the surface towards either the center or the periphery of the disk, or by a "doctor" which lifts the layer to a platform from which it is removed by a screw conveyor. These driers may be enclosed to prevent dusting or contamination of the air with poisonous materials.

When a low temperature is necessary, and yet rapid drying must be effected, drum driers are placed within heavy walls and a vacuum maintained.

Since the rate of evaporation is dependent upon the rate of heat flow through the drying layer, it is evident that if a low temperature is to exist on the heating surface, the vapor pressure of the evaporated liquid in the surrounding space must be kept low. By maintaining a very low air pressure in the drier, an efficient condenser, and a thin film of material on the drum, material such

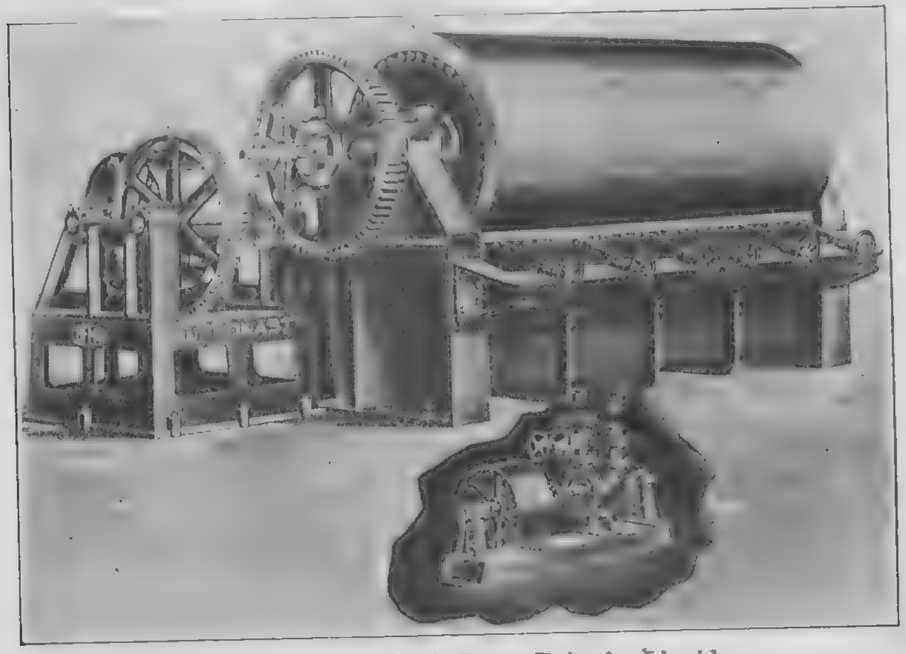


FIG. 114.—Atmospheric Drum Drier for Liquids.

as whole milk may be dried at a very low temperature and yet with considerable rapidity. If the material will tolerate a high temperature, it is clear that exceedingly rapid drying can be effected by using high-pressure steam and maintaining a high vacuum.

The construction of a continuous drum or rotary *vacuum* drier is a complicated matter, as provision must be made for supplying the feed material and taking away the dry product without breaking the vacuum.

Rotary Driers.—The method of transporting material through a cylindrical reaction chamber by rotating the chamber on its

horizontal axis with the discharge end slightly lower than the feed end is admirably adapted to the design of driers for handling all granular, crystalline or lumpy material which does not under this motion run together or roll itself into larger unit pieces. If the material is not injured by being in direct contact with the products of combustion of fuel, flue gases may be led directly through the cylinder, and very rapid evaporation realized.

Lifting plates or shelves may be fastened to the inside of the cylinder, or shell, running through its entire length parallel to the axis and extending radially towards the center. The rotation of the cylinder continually elevates the material and throws it through the current of hot gas or air, the inclination of the shell moving the charge forward.

A simple form of such a rotary drier consists in a single shell made of heavy steel plate supported on steel tires riveted to it, which rest on rollers held in suitable bearings very much as a cement kiln or a tube mill. It is driven by a gear fastened to the shell which engages a pinion keyed to a driving shaft. The discharge end of the drier is placed in direct contact with a furnace, and the flue gases drawn through the drier either by a stack or a fan. A fan is preferable to a stack because in the latter the gases must be so hot in order to maintain the draft that much heat is carried out of the apparatus, and so far as drying is concerned, unused. An exhaust fan permits excellent control of the supply of heated gases and therefore produces a more uniform product. The installation should be so arranged that in case the drier for any reason stops, the flue gases may be by-passed to a stack and excessive heating avoided. If it is desired to calcine the product as well as dry it, the shell may be lined with fire brick and both operations carried on in the same apparatus.

Counterflow.—In an arrangement of this kind the hot dry gases from the furnace meet the charge as it leaves the drier, rapidly taking up any moisture that still remains in it. These gases leave the drier when in contact with the cold and wet charge, thus fully utilizing their heat and moisture-carrying capacity. This is as it should be. But there may be two disadvantages to this counter-current arrangement. *First*, the charge may be heated excessively, and possibly ignited or otherwise injured (as for example, coal); and even if it does not suffer from the high temperature, heat is carried away with the hot charge and lost.

Second, there is a minimum of heat at the feed end where the greatest amount is needed for preheating the entering cold charge and effecting prompt evaporation. Thus a material originally lumpy, may carry so much moisture that a very slight increase in water content through condensation from the air will reduce it to a paste or make it ball together. In counter-current flow the air can become so saturated with moisture in the middle or evaporating zone that it will deposit water when it strikes the cold incoming charge. It is in this case necessary to sacrifice the heat economy of the apparatus to make it operative, if at the same time it is to remain "fool-proof." The difficulty may be met by feeding the drier at the furnace end, *i.e.*, by the use of parallel flow. The fresh charge now comes in contact with the hot dry gas and later condensation upon it through a fall in temperature is avoided. If, in counter-current flow the above condition is met it may be remedied by either increasing the flow of air through the drier, or cutting down the rate of feed.

Parallel Flow.—It is sometimes desirable to reduce the moisture content of a material from a high to a low but definite content, and not to dry below this value. In this case parallel flow offers marked advantages, in that it is possible to so regulate the amount of entering flue gas that on account of the resulting humidity and temperature of the exit gases, the moisture content of the charge cannot fall below the predetermined amount.

Reversed Current.—A combination of the good points of both systems of flow is obtained by passing the flue gases along the outside of the shell parallel to the charge, and bringing them back in the inside counter current to and in contact with the charge. Although the coefficient of heat transfer from the gas to the shell and through this to the charge is smaller than that directly from gas to the charge, nevertheless owing to the great temperature difference at the feed end of the shell, the gas is here materially cooled and the charge heated. The gases meeting the finished charge at the discharge end are still dry, but so reduced in temperature that no ill effects are suffered. It should be noted that even in this type of drier the loss in heat through the discharge of product at a high temperature is frequently very large, and should not be overlooked.

When the drier is placed in the flue from the furnace the flue gas velocities are, in ordinary practice, low, resulting in a low

coefficient of heat transfer to the shell. This objection may be met by constructing the flue so as to be concentric with the shell, at such a distance from it that the velocity of the furnace gases along its surface is relatively high. (See p. 148.) This will reduce the resistance to heat flow as far as possible, and furthermore reduce the area and hence the heat loss from the outside of the flue. Or, two concentric cylinders may be employed, feeding the charge into the space between the shells and passing the flue gases down through the center of the drier parallel to the charge, and back between the shells counter-current to it, Fig. 115. Radiation is reduced by placing the hottest gases on the inside, but obviously a greater heat transfer would be obtained from gases outside a single shell, due to the much greater area exposed, provided the

FIG. 115.—Ruggles-Coles Reversed Current Drier.

gas velocity be kept high by proper flue construction as above indicated. This also results in cheaper and more substantial shell construction.

Notes on Rotary Driers.—Rotary direct-fired driers, both single and double pass as above described, are suitable for drying all materials occurring in aggregates which are not injured by contact with flue gas, or by the relatively high temperature of these gases coming direct from the furnace. Such materials are ores, coal, cement rock, phosphate pebbles and many products of this kind. Where contamination with dust must be avoided, hot air may be used instead of flue gases.

The capacity of such driers is limited by that velocity of the gas in contact with the charge which is allowable without blowing the stock from the drier. This allowable velocity must be determined for each specific material to be dried. Great advantage results from using entering gas at high temperature, since this

enables each pound of gas to pick up a much larger amount of water, thereby reducing the necessary gas consumption, and therefore greatly increasing the capacity without exceeding the allowable gas velocity. For materials uninjured by heat the temperature of the gas is limited by the danger of warping and corroding the shell. Entering gas at 1400° F. can be employed without danger in this regard, especially if the temperature of the shell at the point of gas entrance be kept down by contact with the wet charge as in parallel current and reverse-current operation.

Such driers cannot be operated with sticky materials. Materials sticky while wet, but non-sticky and reasonably absorbent when dry, can be successfully handled in such rotary driers by shunting a portion of the dry, discharged material back to the feed end of the drier and mixing it there with the wet material in such proportion as to absorb its moisture sufficiently to render it non-sticky. The mixture then passes through the drier without "balling up" or sticking to the sides. The amount of dry discharge which must be returned for admixture with the wet stock is determined experimentally for each individual case.

In drying certain other materials such as fullers' earth for filtration purposes, kaolin, ocher and products used for pigments, it is not permissible to use direct firing. In this case a single-pass indirect-fired drier is employed. But such a drier may be fitted with flues or ducts on the outside shell through which the fue gases return, and thus become a double-pass drier. These ducts function as the shelves or lifting plates to distribute the charge through the drying space. When a relatively low and well-regulated temperature must be maintained as in drying brewers' grains, cotton seed, cattle foods and other organic material, a bank of steam coils may replace the furnace, the drying taking place solely at the expense of the heat in the air. Or, steam pipes may be set in a header at the lower end of the drier and be carried its entire length parallel to the axis of rotation. The condensed water is drained into the header and by hollow trunnions is periodically expelled. For drying sand and materials used in glass and pottery, or other products which would be injured by the presence of rust, steam-heated rotary driers may be lined with wood.

Spray Driers.—It is sometimes desirable to evaporate a large amount of water and yet quickly produce a dry product. This

requires very rapid vaporization, necessitating the exposure of the largest possible surface at the highest allowable temperature. When the material is not injured thereby, the liquid, preferably superheated, is sprayed under high pressure directly into a rotary drier together with the flame itself from an oil burner or the other source of heat employed in the drier. In place of radial shelves

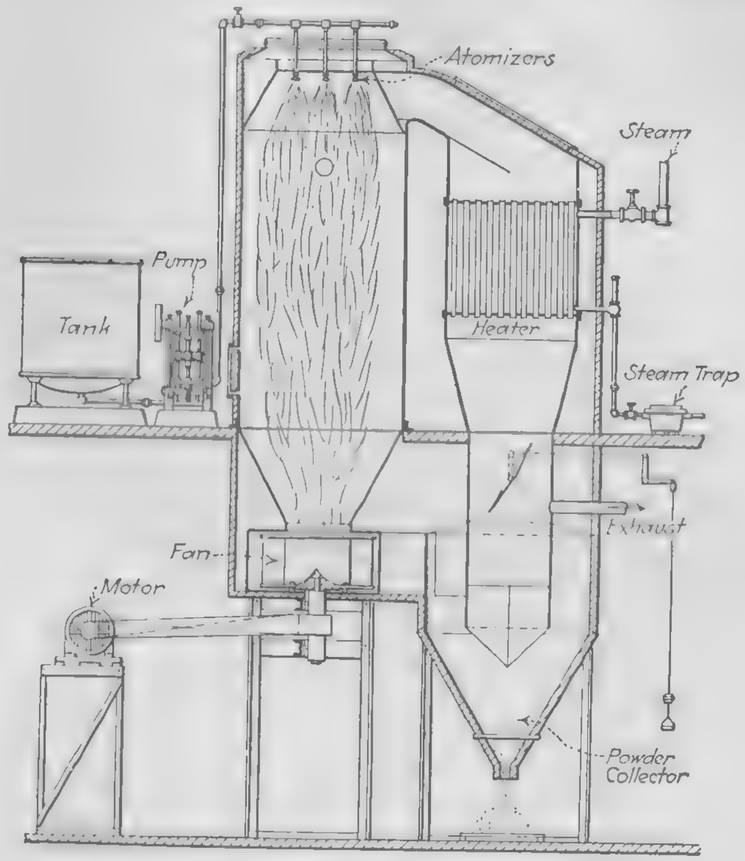


FIG. 116.—Buhl Spray Type Drier.

the drier should be fitted with loose chains hanging horizontally. These keep the surface of the drier clear of adhering material. The product may be so fine as to necessitate an air separator for its total recovery. (See p. 329.) Strong solutions of inorganic salts may be dried in this manner.

If the material be partly organic, as for example, the concentrated liquor from the soda, or sulfate process for making cellulose pulp, the rotary drier may also function as a furnace, and the

material be not only evaporated and dried but also calcined in the one operation.

Driers have been proposed in which the material (solution or emulsion) is sprayed into a chamber through which superheated steam is recirculated, as in Fig. 116. The heat transfer does not here take place under favorable conditions and therefore the use of such an apparatus is limited to the drying of liquids sensitive to air when hot.

Superheated Vapor.—Superheated vapor as a means of carrying heat adapts itself admirably to the drying of material which cannot come into contact with air, and which is itself a poor heat conductor. Thus where wool or leather has been degreased by treatment with naphtha it is hard to dry because of the difficulty in getting the heat necessary for the vaporization of the solvent from steam pipes or other heating surface into the material. By circulating a current of superheated naphtha vapor through the mass, the liquid naphtha is volatilized and carried out of the drier. An amount of vapor equal to the liquid vaporized is continuously drawn off to a condenser, and the material left practically free from all naphtha vapor. This method of drying seems capable of wide application when the material is not so difficult to handle as the above, but where the liquid is to be recovered.

AUXILIARY OPERATIONS AND EQUIPMENT

Most driers utilize air drawn from the room, which is usually warmer than the outdoor temperature. However, the drier in reality utilizes outdoor air, because artificial heat must be employed to bring the outdoor air up to room temperature, and any air taken from the room by the drier must be replaced from outside. In cold weather this means an excessively large heat consumption to bring the outdoor air up to the drier temperature. While the air thus secured is very dry the advantage due thereto is not sufficient to compensate the large heat consumption necessary to warm it.

Recuperation of Heat.—In order to avoid this difficulty three remedies are available. The least satisfactory is the utilization of the waste heat in the exhaust air by a "recuperator" for preheating the incoming air. This method has the advantage of

conserving the low humidity of the outside air without sacrificing heat efficiency, but, owing to the very low coefficient of heat transfer from gas through metal to air (p. 148) the size of the "recuperator" is excessive. Furthermore, the water condensed from the moist, waste air may cause rapid corrosion of the cooling surface.

Recirculation of Air.—The second device involves the use of a closed air circuit in the drier, the wet exhaust air being dehumidified by cooling, either by means of cooling pipes or by water sprays, this cooled air then being reheated and recirculated to the drier. When the waste air from the drier is nearly saturated, this system is highly satisfactory; when, however, the air traveling through the drier picks up but little moisture—a condition encountered toward the end of intermittent drying operations—the quantity of air which must be cooled and reheated is so large that the heat efficiency is very low. Under such conditions resort is best made to a third method, namely, the removal from the waste air of a proportion of it which is thoroughly cooled and dehumidified. This dry fraction is then again mixed with the remainder of the wet air, reducing its humidity to the desired point by dilution. By this device it is possible to realize good heat economy.

Automatic Control of Air Temperature.—The maintenance of automatic control of temperature and humidity is of great importance in drying operations. This is done by the utilization of thermostatic regulators, devices which consist of a sensitive element exposed to the temperature it is desired to control, and which produce some sort of physical effect that can be utilized to regulate the heat supply. Some regulators employ as the sensitive element a metal, the expansion of which operates the mechanism; others use the expansion of a liquid; others the change in resistivity of an electrical conductor; and so on. Some operate through direct mechanical devices while others function electrically. Regulators can be obtained on the market which are simple in construction and maintenance, and which will easily control the temperature within five degrees Fahrenheit. Indeed, control within one degree is realized in commercial practice, though generally the closer the control, the more complicated the mechanism and the more attention it will require. To avoid localized variations in the conditions of the air, it is important to insure perfect

mixing of the air before it reaches the sensitive element of the regulator.

Automatic Control of Humidity.—Thermostatic regulators operate solely to maintain a definite temperature. They can, however, be employed to maintain any desired humidity by utilizing them as wet and dry bulb thermometers. If the sensitive element of a regulator be covered with a wick, kept moist, and exposed to air at a sufficiently high velocity, the element assumes the wet bulb temperature. Any variation in the wet bulb temperature will cause the regulating mechanism to function.

If, for example, it be desired to supply a drier with air of 30 per cent humidity at 100° F., it can be automatically done as follows: The outdoor air employed is passed through a bank of steam coils, and in addition a steam jet blowing live steam into the air preferably just as it enters the heating coils is provided. The valve controlling the steam supply to the heating coils is operated by a thermostatic regulator the element of which is placed at the entrance to the drier and set to function at 100°. The live steam supply to the jet is controlled by a second valve operated by a second sensitive element placed beside the first, but this second element is surrounded by a wick kept wet, and its regulator set to function at 75°. If the air entering the drier be too cold, the first thermostatic regulator will increase the steam supply in the heating coils, thereby raising the temperature of the air. If the wet bulb temperature of the air entering the drier be too high, the second thermal regulator will reduce the steam supply to the jet, thereby reducing the moisture content of the air and, in consequence, its wet bulb temperature.

A still more satisfactory method of controlling the humidity of the air entering this drier is to mix the relatively dry outdoor air with the humid, waste air from the drier itself. In such a case, the wet bulb regulator controls the damper in the duct leading the waste air return to the air entrance of the drier; the dry bulb regulator controls, as before, the steam coils in the air-feed duct. If the dry bulb temperature of the air entering the drier be too low the regulator turns on more steam. If the wet bulb temperature be too high the regulator closes the damper in the wet air return pipe, thus giving a larger proportion of dry outside air.

A device frequently employed for humidity control in driers operating with a closed air circuit is to control the temperature

to which the recirculated air is cooled. The recirculated air is obviously at its dew point after passing through the dehumidifying apparatus, whether this be of the spray type or with metallic cooling surface. The temperature of this air, therefore, determines its moisture content. Thus, in the Tiemann drier (see p. 493), humidity control is obtained by two regulators; the first controlling the dry bulb temperature (dew point, in this case) of the recirculated air as it leaves the spray coolers; and the second the dry bulb temperatures of this same air after being heated by its passage through the steam pipes just previous to coming in contact with the wood. While giving excellent humidity control, it must be borne in mind, as shown above, that this method involves low heat efficiency unless the air discarded from the drier be nearly saturated.

Air Circulation.—One of the most important points in the design of drying apparatus and the control of drying operations is the provision for adequate and uniform air velocity past the material. Especially in the drying of thin sheets and fine grains or lumps a reasonably high velocity is desirable to secure most rapid evaporation. In the case of thicker sheets and larger lumps high velocity does not help so much because, as will be shown on page 522, the major resistance to evaporation in such cases is in the diffusion of the moisture from the interior of the material to the surface. Even in these cases, however, *uniformity* of air distribution past the surface is essential to secure uniform drying. This requires the avoidance in design of sharp bends, especially at those points where the air enters the drying apparatus, of inequalities in cross-section, and the like.

Where the total amount of air required for drying is small, but the velocity past the material must be relatively large, it is highly desirable to use *transverse* circulation of the air over the material, so that the air flows through the apparatus in a spiral path, as illustrated on p. 548. Such circulation involves additional fans, but secures both rapidity and uniformity of evaporation.

In the drying of sheet materials the air must of necessity flow parallel to the sheets. The air impinging against the edges of the sheets dries those edges far more rapidly than the middle, resulting in warping of the sheets due to unequal shrinkage. This can be avoided by protecting these edges from the air. For example,

the sheets may be supported on wire gauze fastened to a frame made of wood or angle iron, the sides of which serve as protection for the edges of the sheet.

For the circulation of air through a drier the pressure drop is usually large while the volume of air required is small. It is consequently advisable to utilize centrifugal fans designed for these conditions. For the *transverse* circulation of air within the drier itself, in order to secure high air velocity past the material being dried, a very large volumetric capacity is desirable. In order to limit the power consumption and the initial cost of the fan the recirculation should be carried out in such a way as to introduce a negligible resistance to the air flow, thus making it possible to employ the so-called " volumetric " type of fan, *i.e.*, a fan with propeller blades, which drive the air in a direction parallel to the axis of the fan. Such fans can be used only against very small pressure heads, but under these conditions handle large volumes at good efficiency and with low initial cost.

PART FOUR: DESIGN OF DRIERS

Steps to be Taken in the Design of Air Driers.—The steps taken in the design of apparatus in which a solid is dried *by means of air* are eight in number and may be taken in the following order.

1. Choose the type of drying apparatus and the drying conditions to be employed, *using the highest safe temperature.*

2. Sketch diagrammatically the apparatus chosen, indicating amounts, moisture contents and temperatures of the material entering and leaving the apparatus, and the temperatures and humidities of the air entering and leaving, and where possible at other points in the drier.

3. From a knowledge of the capacity desired, calculate the air required to carry away the water vapor. Complete details of this step are given on pp. 457 to 458.

4. Calculate the necessary heat supply, making suitable allowance for heat necessary to vaporize the water, heat carried out in stock and conveyors, and heat losses to the surroundings (pp. 457 to 458).

5. Choose suitable methods and devices for controlling the temperatures and humidities of the air at the various points in the equipment (pp. 504 to 507), and indicate these in the sketch.

6. Calculate the time necessary for the escape of the moisture, and the cross-section and length of the drier.

7. Calculate the necessary heating surface, and arrange it so as to maintain the desired drying conditions.

8. Calculate the pressure drop and fan horsepower necessary to maintain the circulation of air.

Characteristics of Drying Apparatus.—The following classification of driers is based upon the methods used in supplying the heat to the charge, these methods depending mainly upon the sensitiveness to heat of the material being dried. This classification is useful in choosing the type of apparatus and the drying conditions to be employed (Step 1) and will be used later as a basis for the design of various types of driers.

1. *Steam Heated Drum and Tray Driers. The charge is in direct contact with the surface of a solid heating element, and all heat is received directly therefrom; the temperature of the heating surface is insufficient to injure the charge*—suitable for thick liquids or pastes which become dusty when dry (pigments), or for similar material requiring very rapid evaporation (milk). Low temperature can be secured by the use of vacuum.

2. *Direct-Fired Rotary*[1] *Driers. The drier is heated directly by hot furnace flue gases*—suitable for granular, lumpy, non-dusting materials insensitive to heat.

   A. Direct contact of flue gas with charge.
      (*a*) Flow counter current.
      (*b*) Flow parallel current.
      (*c*) Flow reverse current.
   B. Indirect contact of flue gas with charge.
      (*a*) Flow counter current.
      (*b*) Flow reverse current.

3. *Air Driers for Sensitive Materials.*
   A. Adiabatic driers giving maximum allowable constant wet bulb temperature—suitable for materials sensitive to heat when wet but not when dry (glue, sugar, etc.).
   B. Constant temperature driers, operated at maximum allowable air temperature—suitable for materials sensitive to heat when dry but not when wet (textiles, rubber, etc.).

[1] Tunnel driers could be employed

C. *Controlled humidity driers*—suitable for materials sensitive to humidity conditions.

(*a*) Decomposition results if humidity falls outside definite upper and lower limits: hydrated crystals and materials from which adsorbed water must not be completely removed, *e.g.*, soda lime. Controlled humidity drier with highest evaporation rate consistent with the humidity limits.

(*b*) Material injured by excessive rate of drying, *i.e.*, by excessive humidity difference: lumber, heavy leather, fine paper, ceramics, plastic films, etc. Controlled humidity drier operated to properly limit the evaporation rate. Intermittent driers sometimes are preferable because of more exact control and because the temperature and humidity conditions necessary for maximum safe drying capacity are incompatible with continuous operation.

Definitions.—Referring to the list of steps to be taken in designing driers, it will be seen that some of the steps cannot be taken intelligently without a thorough knowledge of the mechanism of drying, and hence the problem of determining the proper drying time (Step 6) will be discussed first.

Before taking this up it is advisable to define the units in which percentage moisture is to be expressed in order to facilitate calculations in drier design, and to define "drying conditions."

Dry vs. Wet Basis.—The analytical laboratory usually reports percentage total moisture on the *wet* basis, *i.e.*, material containing 10 per cent moisture contains 90 units of weight of bone dry stock and 10 units of weight of moisture. However, in the calculations which follow, it is preferable to calculate percentage water on the *dry* basis. Thus the material referred to above would contain 11.1 per cent of water on the dry basis, namely, 11.1 lbs. of moisture per 100 lbs. of bone dry stock. The latter method reduces all moisture data to a common basis and hence has an advantage over the former method. For example, the water to be evaporated per ton of product to reduce the moisture content from 60 to 20 per cent of water (wet basis) is 2000 (0.80) $(\frac{60}{40}-\frac{20}{80})$ or 2000 lbs. *Throughout the following pages it will be assumed that all moisture data are expressed on the dry basis: the lbs. of total water per lb. of bone dry stock will be designated by the symbol T.*

Equilibrium Water or "Regain."—As shown on p. 488, certain materials hold definite and appreciable percentages of moisture when exposed indefinitely to air of a given relative humidity. This adsorbed water is called the "equilibrium" moisture, and in industry, the "regain." The lbs. of equilibrium moisture per lb. of bone dry stock will be called the "equilibrium moisture" and designated by the symbol E.

Free Moisture.—The total moisture (T) less the equilibrium moisture (E) is defined as the *free* moisture or *free* water, W, and it will be seen that this difference, $T-E$, is one of the important factors controlling the rate of drying.

Drying Conditions.—The rate of evaporation of moisture from a material is determined by the temperature and humidity of the air with which it is in contact, by the character of its exposure to that air, by the velocity of the air passing it, and by any radiant heat it may receive, *i.e.*, by the *condition of its surroundings*. These external conditions are called the *drying conditions* to which the material is exposed.

Basic Differential Equations for Air Drying of Solids Under Constant Drying Conditions

First, differential equations will be derived for the air drying of solids *under constant drying conditions*. In some cases the equations so derived may be used for commercial driers without introducing serious error. In other cases, it will be shown how these equations must be modified for *variable drying conditions*.

For the purpose of derivation consider a sheet material freely and equally exposed on both sides to the drying air, the drying from the edges being negligible compared to that from the sheet as a whole. The area of either side is A, the total thickness is L and the *actual* water concentration at any point at a given time θ is w units of weight of *free* moisture per unit volume of wet stock. Let Fig. 117 represent a cross-section of the sheet, the lines CD and FG representing the surfaces exposed to the drying air.

The *actual* concentration of free moisture, w, is plotted as ordinates from the base line CHF. Using the subscript 0 to

refer to the start of the drying operation (that is, when $\theta=0$), the initial *actual* concentration of free moisture, w_0 is represented by the line GJD, since the initial concentration is uniform. The total free moisture content of either half of the sheet from the center line to the surface is then $(A)\,\frac{(L)}{(2)}\,(w_0)$, namely, the area $DJHC$. After drying has begun the actual concentration of free moisture at the center line will be represented by some point such as M and the free moisture concentration on the surface will be lowered to some value w_s, corresponding to the point N. If, as is usually the case, the drying operation is suspended before all the free moisture is removed, the actual final concentration will be represented by some line such as QR. Analogous conditions exist on the opposite side of the center line.

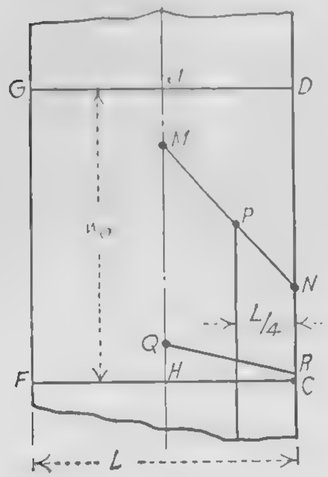


Fig. 117.

The exact integration of the rigorous differential equation[1] is very involved. For all practical purposes it is allowable to assume a *constant* concentration gradient, *i.e.*, that the line MN on Fig. 117 is straight, as shown. Under these conditions the *average* free moisture concentration y (units of weight per unit volume of stock) for the sheet is represented by the point, P, which is a distance $L/4$ from the center line of the sheet, while the *actual* surface concentration is w_s. The total amount of water

[1] In terms of the differential calculus, Newton's law of diffusion states that the partial differential of concentration with respect to time, $\delta w/\delta\theta$, is proportional to the rate of change of concentration gradient with the distance out from the center line to the section where the gradient is taken. At a distance z from the center line of the sheet, the concentration gradient for a section of differential thickness, δz, is $\delta w/\delta z$, and hence the rate of change of gradient with the thickness is $\delta^2 w/\delta z^2$.

Hence

$$\frac{\delta w}{\delta\theta}=C\frac{\delta^2 w}{\delta z^2},$$

where C is the proportionality coefficient, which is determined by the nature of the material, the drying conditions, and units employed.

diffusing to the surface per unit of time from the half sheet is then directly proportional to the area (A) and directly proportional to the driving force, or concentration difference, $y-w_s$, and inversely proportional to the average length of path $(L/4)$. Calling (α) the coefficient of diffusion through the stock at the definite stock temperature in question,

$$\frac{(\alpha)\,(A)\,(y-w_s)}{L/4}=\text{water lost by diffusion/per unit time.}\quad(1)$$

The amount of moisture evaporated from the surface per unit of time under constant drying conditions is directly proportional to the surface exposed and to the wetted fraction of this surface. Assuming the wetted fraction to be proportional to w_s,

$$(\beta)\,(A)\,(w_s)=\text{water lost by evaporation per unit time,}\quad(2)$$

where β is the coefficient of surface evaporation for the constant drying conditions.

If the surface of the sheet be considered as a layer, indefinitely thin, it is obvious that it can contain only an infinitesimal quantity of water. Any evaporation from the surface must, therefore, deplete the water content of the surface layer unless diffusion from the interior is sufficient to compensate therefor. Since the water content of this surface layer is infinitesimal, it means that diffusion must quantitatively compensate for evaporation in order to keep any water whatever on the surface. In other words the two quantities above are equal, *i.e.*, Eq. (1) = Eq. (2). Since also, the only water lost by the sheet is by evaporation, it means that the loss in moisture per unit time, namely, the rate of change of average concentration per unit volume $(dy/d\theta)$ multiplied by the total volume, $(A)\,(L)/(2)$, is equal to both the above expressions, namely,

$$-\frac{(dy)\,(A)\,(L)}{(d\theta)\quad(2)}=\frac{(\alpha)\,(A)\,(y-w_s)}{L/4}=(\beta)\,(A)\,(w_s)\quad\ldots\quad(3)$$

By eliminating[1] w_s from this equality, and canceling out the area

[1] $-\frac{dy}{d\theta}=\frac{8\alpha y-8\alpha w_s}{L^2}=\frac{2\beta w_s}{L}$, $\quad 8\alpha y-8\alpha w_s=2\beta L w_s$,

whence

$$w_s=\frac{4\alpha y}{4\alpha+\beta L},\quad\text{and}\quad -\frac{dy}{d\theta}=\frac{2\beta w_s}{L}=\frac{8\alpha\beta y}{L(4\alpha+\beta L)}.$$

term, which appears in the numerator of all three equalities, one obtains

$$-\frac{dy}{d\theta}=\frac{8\alpha\beta y}{L\,(4\alpha+\beta L)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is the basic differential equation for the air drying of solid materials *under any one definite set of drying conditions.*

As already indicated, the coefficient of diffusion (α) varies with the temperature of the stock; this coefficient would be expected to increase with the temperature of the stock, because the fluidity of water increases with temperature (see p. 142). Furthermore, as shown on p. 487, the coefficient of surface evaporation (β) is a function of air velocity (v) and the difference of vapor pressures of water on the surface of the sheet and that in the surrounding air. Hence $\beta=f(v)(p_s-p_a)$, where $f(v)$ represents an experimentally determined function of average "mass velocity" (for the particular material and arrangement of stock) and p_s and p_a are the corresponding vapor pressures of water on the sheet surface and in the drying air. Since the average concentration of free moisture (y) appears on both sides of Eq. (4), it is allowable to substitute for y the weight ratio of free moisture on the dry basis, $(T-E)$. Hence the basic differential equation for the air drying of a solid material may be written as follows, for any set of constant drying conditions:

$$-\frac{d\,(T-E)}{d\theta}=\frac{8\,(\alpha)\,(\beta)\,(T-E)}{(4\alpha+\beta L)\,L}=K\,(T-E), \quad . \quad . \quad (5)$$

where K is the drying coefficient for any definite set of drying conditions, $\beta=f(v)(\Delta p)$, and α increases with the temperature of the sheet.

Eq. (5) *indicates that the rate of drying at any instant under any definite drying conditions is independent of the area of surface of the material being dried, and is proportional to the percentage of free moisture on the dry basis.* This differential equation is complicated and must be integrated before the drying time can be calculated. When integrating, it should be remembered that α and β are variables, which may be considered as constants only for any one definite set of *constant drying conditions.* It is integrable exactly in a large number of special cases, some of which are very simple; otherwise the differential equation may be

applied to successive stages of the drying period. Further development of this equation will be given under each special case. It is essential that the reader understand the derivations and keep clearly in mind the assumptions made; hence the limitations for the equation just derived will be reviewed before proceeding to the special cases.

Limitations to Eq. (5).—(1) The water is diffusing only in the direction normal to the exposed surface, and through a cross-section of constant area.

(2) The drying conditions are identical on both sides of the material. (For drying from one side only, see pp. 517 and 522.)

(3) Rate of surface evaporation under constant drying conditions is proportional to the fraction of surface wetted, which in itself is proportional to the free moisture concentration.

(4) During the drying, the moisture concentration is at a maximum at the center of the sheet, decreasing linearly to the value on the surface.

The *first* case is found in the drying of large sheets or trays of material where the area of the edges is negligible compared to that of the sides. It also holds where the area of the edges is not negligible to that of the sides, when the edges have been protected in order to avoid drying from the edges. Further, the first condition is met in all cases where the rate of diffusion is very large compared to the rate of surface evaporation, even for materials in lump form. See Special Case I. It would not hold for drying of lumber not protected on the ends, as the rate of diffusion "with the grain" is widely different from that "across the grain."

The *second* case is the general one as it is economically desirable to dry from *both sides* of the sheet. However, in case of drying from one side only, where the moisture concentration is a maximum at the protected face, decreasing linearly to the value on the surface, a derivation similar to the one above gives:

$$-\frac{d\,(T-E)}{d\theta}=\frac{2\,(\alpha)\,(\beta)\,(T-E)}{L\,(2\alpha+\beta L)}. \quad . \quad . \quad . \quad . \quad (5a)$$

The *third* case is general provided the per cent water is not too high. See Fig. 118. Where the water concentration is greater than the "critical" value, *i. e.*, to the right of the point A, the whole of the surface is wet and hence evaporation pro-

ceeds *at constant rate* until the critical point is reached, after which the rate of drying decreases with the average free moisture content as called for by Eq. (5), the rate becoming zero at the point C, which corresponds to the per cent equilibrium moisture. However, as emphasized elsewhere, when the per cent water is high, it is sometimes possible to remove a large proportion of the water mechanically, *i.e.*, by the use of pressure, which is a more

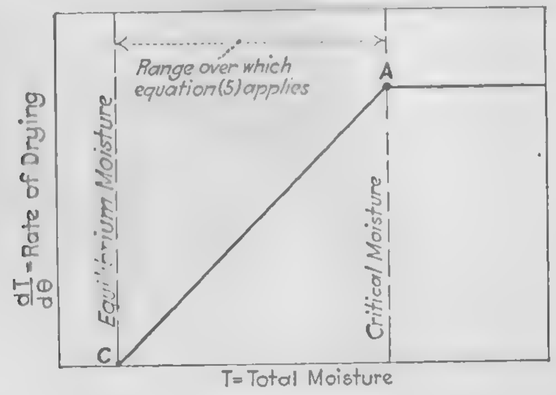


FIG. 118.

economical method of drying than by the process of vaporization.

The *fourth* case is found in the drying of materials such as vegetable tanned and chrome leather, twine, heelboard, paper, and the like. It does not apply to materials such as soap and lumber, and hence in the latter case the above equation must be modified to allow for this fact. This will be treated under "*Skin Effect*," see Case III.

CASE I. DIFFUSION RAPID COMPARED TO SURFACE EVAPORATION

In the case of materials through which the moisture diffuses rapidly, owing to their capillary character, such as paper, heelboard, and the like, the term (4α) may be so large in comparison to (βL) that the latter term may be neglected. This condition occurs where α is very large, where L is very small, and where

(4α) is large in comparison to (βL). Under such conditions Eq. (5) becomes

$$-\frac{d\,(T-E)}{d\theta}=\frac{2\,(\beta)\,(T-E)}{L}. \quad . \quad . \quad . \quad . \quad . \quad (6)^1$$

Equation (6) *indicates that the instantaneous rate of loss of free moisture for any particular set of constant drying conditions is directly proportional to the free moisture content at that time and inversely proportional to the thickness. If some other set of constant drying conditions be employed, the value of* β *will change, as it is a function of air velocity and partial pressure difference.*

(*a*) **Shrinkage Negligible.**—If the material does not shrink on drying L is a constant for any particular drying run, and *for constant drying* conditions Eq. (6) may be integrated between limits, the subscript 0 referring to zero time, giving:

$$\log_{10}\frac{T_0-E}{T-E}=\frac{2\,(\beta)\,\theta}{2.3\,L}=\frac{2f\,(v)\,(\Delta p)\,(\theta)}{2.3\,L}=K\theta. \quad . \quad . \quad (7)$$

Equation (7) *indicates that the drying time for various runs under the same constant drying conditions is directly proportional to the logarithm of the ratio of the initial and final free moisture and directly proportional to the thickness.* For example, if for a given material *under constant drying conditions* one hour is required to reduce the per cent free water (on the dry basis) from 100 to 50, one hour more will be required to reduce it from 50 to 25, since the ratio of 100 to 50 is the same as the ratio of 50 to 25. If the thickness were halved, the time required for the same drying as above would be halved.

(*b*) **With Shrinkage.**—Before integrating Eq. (6), it is necessary to allow for the fact that L is a function of the free moisture content.

Experiments on *certain* materials show that the thickness L

[1] If the material is dried from one side only,

$$-\frac{d(T-E)}{d\theta}=\frac{\beta(T-E)}{L}.$$

Note that the rate of drying for this case is only *one-half* that obtained by drying from *both* sides of the sheet.

at any time may be satisfactorily represented as a linear[1] function of the free moisture on the dry basis, namely,

$$L = L_e[1 + a(T - E)],$$

where L_e is the thickness corresponding to the equilibrium water content and a is the shrinkage coefficient determined for the particular material in question. Substituting this value in Eq. (6) one obtains

$$-\frac{d\,(T-E)}{(T-E)} - a[d\,(T-E)] = \frac{2\,(\beta)\,d\,\theta}{L_e},$$

which upon integration *for constant drying conditions* between between limits of T_0 and θ_0 and (T and θ) gives

$$2.3 \log_{10}\frac{T_0 - E}{T - E} + a(T_0 - T) = \frac{2\,(\beta)\,\theta}{L_e} = K\theta. \quad \ldots \quad (10)$$

Experimental Verification of Equations for Case I.—Data have been obtained by Drew[2] on heelboard (made from a pulp of ground leather and paper) under conditions artificially controlled to give constant drying conditions for each run, but with variation of the conditions from one run to another. These will be used to illustrate the application of Eq. (10), which may be written

$$2.3 \log_{10}(T - E) + aT = aT_0 + 2.3 \log_{10}(T_0 - E) - \frac{2\,(\beta)\,\theta}{L_e}. \quad (10a)$$

Since all terms in Eq. (10*a*) are constant for a given run except T and θ, if the left-hand side be plotted against time a straight line should result, the slope of which is $K = 2(\beta)/L_e$. For this particular material a is found to be approximately 0.28. Figure 119 shows data of a typical drying run (under constant drying conditions) treated in this manner, and it is seen that the points are satisfactorily represented by a straight line. The lower curve on this figure, marked 2.3 log $(T-E)$, shows the effect of neglecting the term aT.

[1] This linear relationship does not hold for all materials. It is, however, always a good approximation when the variation in moisture content is not too great. When necessary other empirical relationships of sufficient accuracy can usually be found.

[2] *M. I. T. Chem. Eng. Thesis*, 1911.

According to Eq. (10) values of K for runs under constant drying conditions should vary inversely as the thickness, hence a plot of K as ordinates versus $1/L_e$ should give a straight line having a slope of 2β. This is illustrated by Fig. 120.

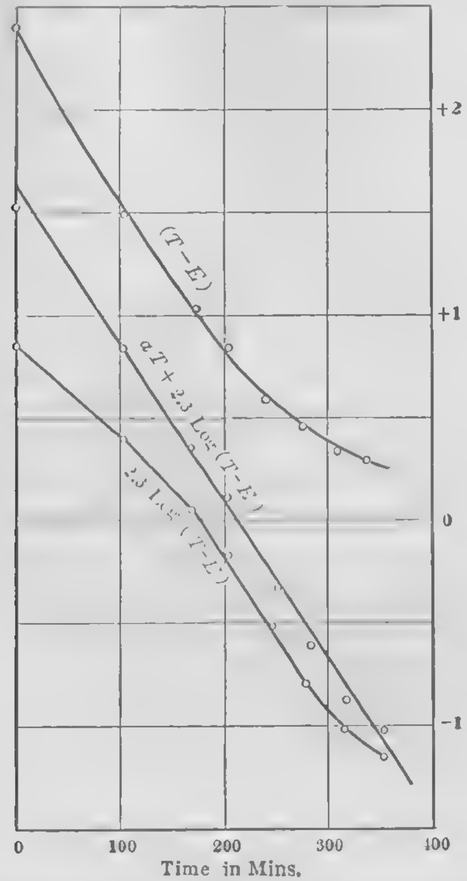


FIG. 119.—Adiabatic Air Drying of Heel-board; Constant Drying Conditions.

As previously stated,

$$(\beta) = [f\,(v)]\,(\Delta p),$$

hence

$$K = \frac{2\beta}{L_e} = \frac{2\,[f\,(v)]\,(\Delta p)}{L_e}.$$

Thus for runs at constant air velocity on material having a constant thickness at equilibrium, the experimental value of K should be directly proportional to Δp, the slope being numerically equal to $(2)[f(v)]/L_e$. This is illustrated by Fig. 121.

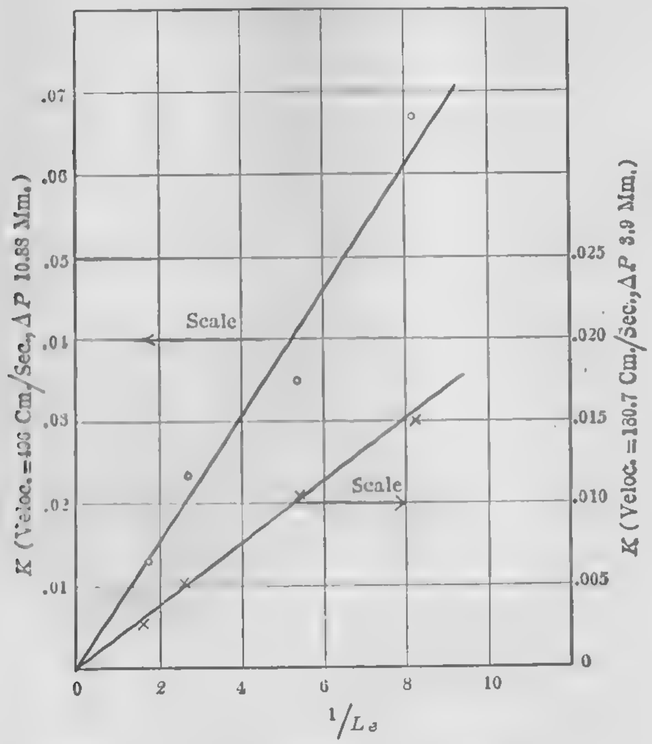


FIG. 120.—Adiabatic Air Drying of Heel-board; Effect of Varying Thickness.

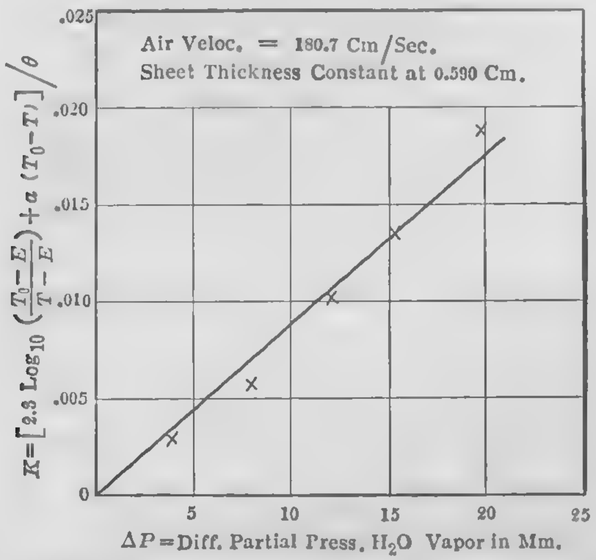


FIG. 121.—Adiabatic Air Drying of Heel-board; Effect of Varying Δp.

The following table shows the constancy of $KL_e/\Delta p = 2[f(v)]$ for runs made at constant velocity (180.7 cm. per sec.) in which Δp and L_e each vary five-fold.

Run No.	K	L_e	Δp	$KL_e/\Delta p$
1	0.0031	0.585	3.9	0.00047
2	0.0051	0.395	3.9	0.00052
3	0.0107	0.184	3.9	0.00051
4	0.0151	0.123	3.9	0.00048
5	0.0059	0.615	8.0	0.00045
9	0.0103	0.590	12.1	0.00050
13	0.0134	0.581	15.1	0.00052
17	0.0188	0.586	19.7	0.00056

Figure 122 indicates the effect of air velocity on K for runs made with constant Δp and L. It is seen that in this case, $2[f(v)]$ may be satisfactorily represented by a 0.36 power of the

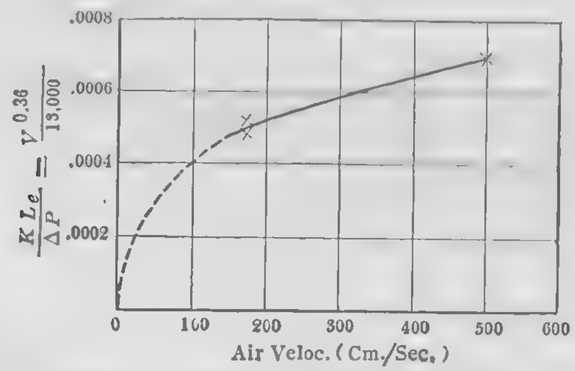


FIG. 122.—Adiabatic Air Drying of Heel-board; Effect of Air Velocity.

superficial velocity. The equation showing the combined effect of air velocity, v (cm. per sec.), Δp (mm. of mercury) and L_e (thickness in cm. at equilibrium moisture content) for this material is as follows:

$$2.3 \log_{10}\frac{T_0-E}{T-E}+0.28\,(T_0-T)=\frac{(\Delta p)\,(v)^{0.36}\theta}{13{,}000\,L_e}, \quad . \quad . \quad (10b)$$

where θ is in minutes and T and E are expressed as lbs. of water per lb. of bone dry stock.

Case II. Diffusion Slow Compared to Surface Evaporation; No Skin Effect

In the case of materials through which moisture diffuses slowly, the term 4α may be so small in comparison to βL that 4α may be neglected. Under such conditions Eq. (5) becomes

$$-\frac{d\,(T-E)}{d\theta}=\frac{8\,(\alpha)\,(T-E)}{L^2}. \quad . \quad . \quad . \quad . \quad (11)^1$$

The drying rate in this case is directly proportional to the free moisture, but is inversely proportional to the square of the thickness. As will be shown on page 527, α increases with stock temperature.

(*a*) **Shrinkage Negligible.**—For this case L is independent of free moisture, and Eq. (11) becomes on integration for *constant drying conditions* (*i.e.*, for constant stock temperature),

$$\log_{10}\frac{(T_0-E)}{(T-E)}=\frac{8\,(\alpha)\,(\theta)}{2.3\,L^2}=K\theta. \quad . \quad . \quad . \quad (12)$$

Eq. (12) *states that the drying time is directly proportional to the square of the thickness and the logarithm of the ratio of the free moisture in the stock at the start to that at the end of drying.*

Experimental Verification of Equations for Case II.—These equations, (11) and (12), may be applied to the drying of twine on a steam-heated drum, using the data of Maverick and Webster.[2] In Fig. 123 the total moisture is plotted against the time twine is on the drum. From this curve $dT/d\theta$ is read off graphically at each point, and plotted against total moisture, as in Fig. 118, p. 516; the value of E is equal to the abscissa at which $dT/d\theta$ becomes zero. In order to determine K one may plot the logarithm of the free moisture against the time, as in Fig. 124.

Fig. 125 shows the value of the drying coefficient for twine plotted against the inverse square of the diameter of the cord, showing that the slope is constant within the experimental

[1] If the material be dried from one side only,

$$-\frac{d(T-E)}{d\theta}=\frac{2\alpha(T-E)}{L^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11a)$$

Note that the rate of drying in this case is only *one-fourth* that obtained when drying from both sides of the sheet.

[2] *M. I. T. Chem. Eng. Thesis*, 1916.

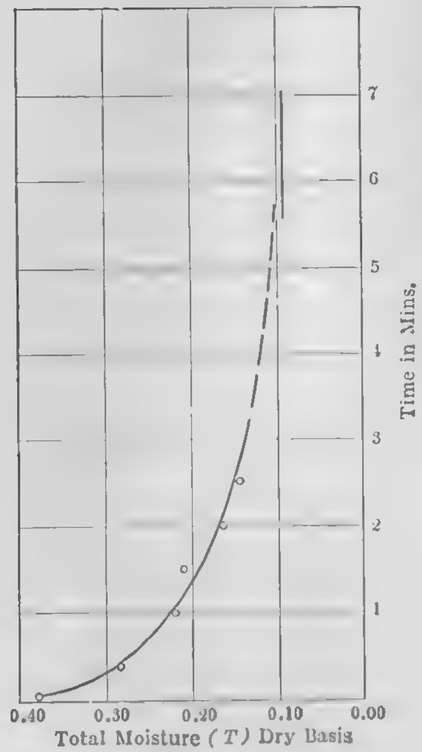


Fig. 123.—Drying of Twine.

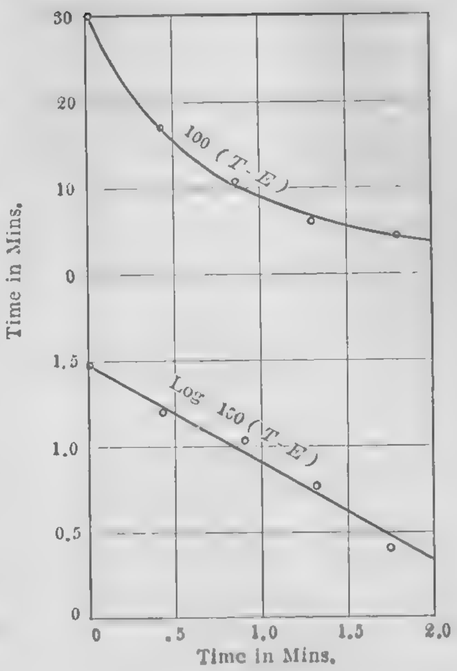


Fig. 124.—Drying of Twine.

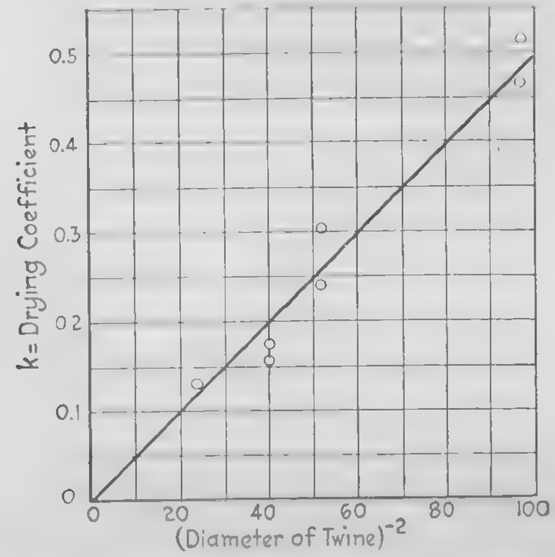


Fig. 125.—Drying of Twine; Effect of Thickness.

error. The coefficient of diffusion (α) is known to vary with the stock temperature, and the variation of individual points from the line in Fig. 125 may be due to the fact that the stock temperature did not remain absolutely constant. For this case the drying equation is

$$\log_{10}\frac{T_0-E}{T-E}=K\theta=\frac{0.005\theta}{D^2},$$

where D is the diameter of the twine in inches and θ is in minutes.

(*b*) **Shrinkage not Negligible.**—When there is appreciable shrinkage, Eq. (11) cannot be integrated until allowance is made for variation of thickness with free moisture. When the thickness is a linear function of the free moisture, namely,

$$L=L_e[1+a(T-E)]$$

Eq. (11) becomes on integration for *constant temperature of stock:*

$$2.3\log_{10}\frac{T_0-E}{T-E}+2a\,(T_0-T)+\frac{a^2}{2}(T_0^2-T^2)=\frac{8\,(\alpha)\,(\theta)}{L_e^2}. \quad (13)$$

If the variation of L with $T-E$ be not satisfactorily represented by a linear function, some other empirical relation should be obtained and substituted into Eq. (11), which upon integration will give a form different from Eq. (13). In choosing the empirical function between L and $(T-E)$, it is obviously desirable to employ one which will make the integrated form as simple as possible and yet represent the data with sufficient accuracy.

The equations given above (Special Cases II*a* and II*b*) must not be used for very thick materials, as the "skin effect" may develop under such conditions, and this necessitates the use of the equations given under Special Case III.

Case III. Rate of Diffusion of Moisture is Slow Compared to Rate of Surface Evaporation; with Skin Effect

In the drying of certain classes of materials equally exposed to air on both sides, it was assumed that the moisture concentration gradient was linear, decreasing from a maximum at the center line of the sheet to the value on the surface. It has been seen that equations derived on this basis are substantiated by drying data for certain materials.

In the drying of relatively thick sheets of certain materials (wood, soap, glue, jellies, etc.) such a diffusion gradient is not quickly set up, and hence, under such conditions, the basic differential equations must be modified. Fig. 126 represents a cross-section of a sheet of original thickness L.

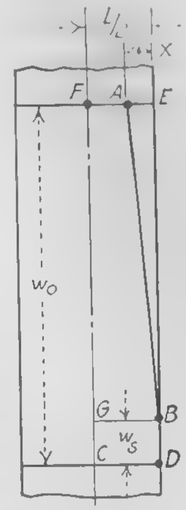


Fig. 126.

Plotting *actual* concentrations (w) of *total* moisture above the base line, CD, CF represents the initial actual concentration (w_0).

Diffusion of water will start, the gradient after the elapse of the time θ being as shown by the line AB; as the drying proceeds further A moves towards the center line of the sheet along the line EF. Call the thickness AE through which the diffusion is taking place at this time x. This distance x is a variable in the following equation which states the equality of the instantaneous rate of loss of moisture to the rate of diffusion of moisture, namely:

$$-\frac{(dw)\,(A)\,(L)}{d\theta\,(2)}=\frac{(\alpha)\,(A)\,(w_0-w_s)}{x}. \quad . \quad . \quad . \quad (14)$$

The layer of thickness x $(=AE)$ produces what is called the skin-effect of the drying operation. Usually the dried portion on the surface will have a different appearance or feel than the undried interior, and hence an inspection of a sample of partially dried material will reveal whether the skin effect has developed.

In Fig. 126

$$w_0=\text{area } FEDC,$$
$$w_s=\text{area } GBDC,$$
$$w=\text{area } FABDC,$$
$$w_0-w=\text{area } AEB=(AE)\,(BE)/2,$$
$$w_0-w_s=\text{area } GFEB=(FE)\,(BE).$$

Hence,
$$\frac{w_0-w}{w_0-w_s}=\frac{(AE)}{(2)\,(FE)}=\frac{x}{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Substituting value of x from Eq. (15) in Eq. (14) one obtains:

$$-\frac{dw\,(w_0-w)}{d\theta}=\frac{(2)\,(\alpha)\,(w_0-w_s)^2}{(L)^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Inasmuch as analyses of the material for moisture give the *average percentage* of water instead of the *actual concentration*, it is desirable to introduce the former units in Eq. (16) instead of the actual concentrations there given.

Calling the *average total* moisture on the dry basis at any time, T, the initial value is T_0, the value on the surface is T_s, the value corresponding to equilibrium moisture is E, and the decrease in a differential time $d\theta$ is dT.

Now $$\frac{dw\,(w_0-w)}{(w_0-w_s)^2}=\frac{dT\,(T_0-T)}{(T_0-T_s)^2}.$$

Hence Eq. (16) may be written

$$-\frac{dT}{d\theta}=\frac{2\,(\alpha)\,(T_0-T_s)^2}{L^2\,(T_0-T)}. \quad . \quad . \quad . \quad . \quad . \quad (17)^1$$

The term T_0-T is a measure of the extent of the drying at any time, *i.e.*, the loss in weight. Equation (17) states that the instantaneous rate of drying at any time is proportional to the reciprocal of the loss in weight up to that time. Since the loss in weight increases as drying proceeds, this requires that the rate of drying should decrease as the drying proceeds. After the drying has been carried to such an extent that the point A has retreated to point F at the center line of the sheet, the skin-effect equations no longer apply, and those given under Case II should be used. Hence the skin-effect equations apply up to the time that the per cent free water has fallen to half the initial value. Often the drying is carried no further than this.

(*a*) **Without Shrinkage.**—For materials in which the skrinkage is negligible between the moisture limits involved, L may be taken as constant. Since T_0, T_s and α are also constant for any run under constant drying conditions, Eq. (17) becomes upon integration *for constant drying conditions:*

$$(T_0-T)^2=\frac{4\,(\alpha)\,(T_0-T_s)^2}{L^2}\theta. \quad . \quad . \quad . \quad . \quad (18)$$

[1] In case drying occurs from one side only,

$$-\frac{dT}{d\theta}=\frac{\alpha(T_0-T_s)^2}{2L^2(T_0-T)}.$$

Note that in this case the rate of drying is only *one-fourth* that obtained when drying from both sides.

Since it is not convenient to determine T_s by analysis and since the material is drying so slowly that its surface is nearly in equilibrium with the drying air, T_s will be assumed as equal to E, the water on the dry basis as read from the equilibrium curve for the material in question. Because of this assumption, and since the line AB was assumed to be straight, which is an approximation, it is better to substitute an exponent n for the square term appearing on T_0-T in Eq. (18), giving:

$$(T_0-T)^n=\frac{4\,(\alpha)\,(T_0-E)^2\theta}{L^2}=K\theta, \quad . \quad . \quad . \quad (19)$$

where n and α, or n and K, are experimentally determined coefficients. As already indicated, n should be in the neighborhood of 2, and α increases as the temperature of the stock increases. Since the temperature of the stock cannot fall below the wet bulb temperature of the air, and may lie between the wet and dry bulb temperatures, the stock temperature will be greater when *humid* hot air is used than when *dry* hot air is used. Hence where diffusion of the liquid through the stock is the limiting factor, the use of *humid* air will dry the stock faster than *dry* air at the same temperature.

(*b*) **With Shrinkage.**—When L varies with T, it is necessary to derive an empirical relation and substitute the value for L in the differential Eq. (17) before integrating it.

However, the resulting integral will be somewhat complicated, and it is possible to use Eq. (19) which neglects shrinkage, for cases where shrinkage occurs, allowing the experimentally determined coefficients n and α, or n and K, to take care of the error so introduced.

Results of Experiments on Bar Soap.—Figure 127[1] shows a plot of $\log_{10}\frac{100(T_0-T)}{T_0-E}$ versus $\log\theta$ for bar soap and it is seen that the experimental points for a run under constant drying conditions fall on a straight line, as required by Eq. (19). The value of n (the slope of the line) is seen to be about 1.93 for this material.

[1] BUNKER, *M. I. T. Chem. Eng. Thesis*, 1921.

Drying of Solids by Air under Variable Drying Conditions

In the preceding paragraphs differential equations have been derived for the drying of solids by air. These have been integrated for *any definite set of constant drying conditions, i.e.,* by assuming the coefficients α and β to be constant for the constant conditions. The resulting equations have been verified by comparison with experimental data obtained *under constant drying conditions.*

It has been shown that the coefficient of diffusion (α) of liquid water through the stock increases as the temperature of the stock is raised, and that the coefficient of surface evaporation

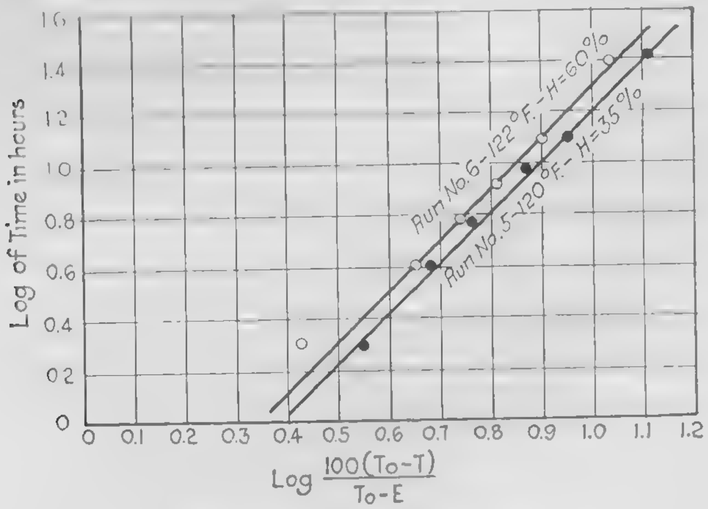


Fig. 127.—Drying of Bar Soap.

(β) varies directly as the pressure gradient (Δp) of water vapor from the surface of the stock to the drying air, and directly as some function of the air velocity. In an actual drier, the drying coefficients may vary, and the problem to be met in the design of a full scale drier involves making proper allowances for the variations in the coefficients. This has been done for various cases (pp. 536 to 556) by inserting in the differential equations given above the value of the drying coefficient involved, as a function of the proper variables, obtaining new integrals for variable drying conditions.

Design of Driers.—Referring to the list of steps to be taken in designing a drier (see p. 508), it is obvious that the only one

presenting any major difficulties is the sixth one, that of determining the drying time.

Having considered the factors upon which drying depends, and the mechanical methods in use for handling material to be dried, it is now desirable to indicate how the fundamental concepts of drying may be applied to the design of suitable apparatus for any given purpose.

Although a knowledge of the physical constants and other properties of a material are essential to an intelligent attack of the subject, it is seldom that these alone are sufficient to enable one to determine the dimensions and conditions for the most efficient operation. It is necessary, therefore, for an intelligent design, to obtain by experimentation upon the material in question the drying coefficients (pp. 511 to 527). It is entirely possible to arrive at these data by experimentation on a laboratory scale, although the larger the scale on which the work is done, the less liable the result will be to error from the omission of factors, present in commercial operation, but not in the laboratory. In these experiments, it is necessary to have operating conditions duplicated as nearly as possible. For example, if the exposure is to be in a rotary drier, the experimental apparatus should be of this type. The size of lump material, thickness of sheet, and its physical condition as to percentage water and temperature should be the same as that which will form the feed of the drier to be designed.

The equations given in the following discussion are to be used therefore, for but two purposes; either the design of commercial apparatus for the drying of a specific material on the basis of coefficients determined from experiments upon the material itself, or to enable one to predict quantitatively the results of changes in either operation or construction of a given drying apparatus handling a definite material. The coefficients in the latter case are determined by studying the actual performance of the apparatus, or the problem is solved by a ratio calculation, in which case the coefficients cancel. An example of a laboratory study of drying conditions and data is given, together with an application of the equations derived.

The subsequent treatment of drier design follows the apparatus classification based on the method of supplying the heat (see pp. 509 to 510).

1. Design of Steam Heated Drum and Tray Driers

The design of driers of this type may be considered conveniently as a problem in heat transfer. As emphasized in the chapter on Flow of Heat one must consider the various resistances met by the heat in flowing from one medium to another. In this case there are three resistances: from condensing vapor to metal wall, that of the wall itself, and from the metal wall to the air in the room. This last resistance really includes three resistances: contact resistance from metal to stock, resistance of stock itself, and from stock to air. Where it is desired to measure the individual resistances, skin temperatures must be taken.

The surface temperature of a material may be obtained by placing a thermo-couple upon the surface, the element having previously been heated to approximately the temperature of the material. By noting whether the element rises or falls in temperature, it is possible to determine whether the material is hotter or colder than the couple; a few trials will enable one to have the couple at substantially the same temperature as the sheet. To prevent radiation the element should be mounted flush with the inner surface of an insulating pad, and the whole pressed upon the surface to be measured. It must not be kept in contact with this surface for any great length of time because the pad will prevent evaporation and will therefore cause a local rise in the surface temperature of the sheet.

(*a*) **Drum Driers for Solids.**—Textiles are frequently dried by passing them over a series of hollow metal drums provided with means for supplying steam and removing condensate and air. In some cases the steam is passed through several drums in series.

The first resistance (from steam to metal) depends on the percentage of non-condensable gas[1] in the steam (this should be small in good practice), the velocity of the steam, the fraction of the total internal heat transfer surface that is submerged, etc.

The second resistance (that of the wall itself) depends on the thickness and thermal conductivity of the metal used. Where very thick cast-iron rolls are employed, this resistance may be quite an appreciable percentage of the total resistance.

[1] See p. 155.

The third resistance (from drum to the stock, through the stock, and into the air) is usually the greatest of the three resistances. Hence it is clear that design should be based on results of experiments for the type of drier and material in question, conditions in the experiments being as similar as possible to those to be used in production. In a certain drier of this type handling wood pulp the third resistance was about 76 per cent of the total resistance to heat flow. The *overall* coefficient was about 24 B.t.u. per hr. per ° F. per sq. ft. of outer surface.

(*b*) **Drum Driers for Liquids.**—When solutions or suspensions are concentrated or reduced to a solid on a steam heated drum, the film of material in immediate contact with the drum becomes quite dry in a very short time, and this dry inner layer serves as an insulation to separate the more moist layers from the heating surface. The process then reduces to a conduction of heat through the dry layer into that portion which still remains wet. When the rate of heat flow is great the temperature of the sheet will approach the boiling temperature of the liquid at the pressure used. Hence it follows that the use of vacuum in the chamber housing the drum will lower the surface temperature and thus increase the rate of heat flow and consequently the evaporative rate.

(*c*) **Tray Driers.**—Where the material to be dried is placed on trays, the heat may be supplied solely from the air, and in this case special drying equations are available. (See Air Drying of Solid Materials.) Where the trays are supplied with heat other than as described above, as when the trays are placed on hollow shelves or pipes supplied with steam, the problem is conveniently treated from the heat transfer point of view. The resistances here met are similar to those discussed under Drum Driers for Solids. It should be noted that a very important factor is the thickness of the material on the trays.

2. Design of Direct-Fired Rotary Driers

The temperature of the charge in a drier of this type changes with the time of exposure to the drying air as indicated qualitatively by the full line curve, *FABC*, in Fig. 128. During the preliminary period, *FA*, the charge is heating up but evaporation is negligible. Evaporation then takes place in the zone *AB*,

accompanied by a slight temperature rise. Finally the charge is superheated and the last trace of moisture expelled in the period *BC*. If a completely dried product be not desired, the operation is stopped before the point *B* is reached.

The exact determination of this curve would be difficult, but it is a satisfactory approximation to assume constancy of temperature during the evaporative period, *i.e.*, to assume that the temperature of the charge follows the dotted straight lines, *FDEC*, rather than the full curve in the plot. The important point is, therefore, the estimation of the temperature of evaporation, *DE*.

Direct-fired driers always employ high temperature gases and in consequence develop a high rate of evaporation. The tem-

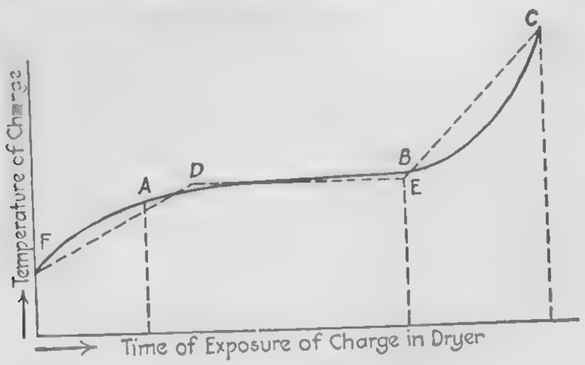


FIG. 128.

perature of the charge therefore, approaches the boiling point, and changes but slightly during the period of evaporation. (See humidity chart, p. 456.) From inspection of the chart it is obvious that, for material so wet that the surface is saturated, the temperature of the charge during the evaporative period when exposed to gases 300° F. and above will be from 110 to 160° F. For lower moisture content, however, the charge temperature increases asymptotically to the boiling point, *i.e.*, to approximately 180° to 210° F. The difference in temperature between the charge and drying air is so great that any reasonable error in estimating the temperature of evaporation will not invalidate the calculations.

The design of such driers resolves itself therefore into a simple calculation of heat transfer, the process being assumed to take place in three separate stages, the preheating, the drying, and the superheating of the charge. In the equation for heat transfer, $Q/\theta = hA\Delta t$, it is not convenient to determine the surface exposure,

A, and hence the term hA is treated as a single coefficient. The value of hA is proportional to the volume of the drier for apparatus of the same type. Obviously the coefficient, hA, must be determined for each material and type of apparatus, from the performance of actual driers, experimental or full scale.

Illustration 1.—A rotary drier is constructed of a steel shell 4 ft. 6 in. inside diameter and 20 ft. long, and rotates at 4 r.p.m. It is drying 12,000 lbs. hourly of a wet ore carrying 16 per cent moisture. The dry ore has a specific heat of 0.18 and is discharged at 240° F. The ore occupies roughly 20 per cent of the volume of the drier. The flue gas flows counter current to the ore, enters at 1065° F. and leaves at 160°. Its Orsat analysis is 3.2 per cent CO_2, 17.3 per cent O_2 and negligible CO. Its dew point at entrance to the drier is 76° F. ($p_{H_2O} = 22.8$ m.m.). The temperature of the surroundings may be assumed 70° F. as a base, and the barometer is normal. Assume the drier to be thoroughly lagged.

Calculate the dry gas in lb. mols passing per hour, the linear gas velocity at the cold end, the heat consumed in evaporation and the heat lost in the dry ore. Design an ore cooler of a type similar to the drier to recover 85 per cent of the heat now lost in the product by preheating the air for the furnace.

Solution.—The heat utilized by the drier is that involved in heating the ore from 70° to 240° F. and in converting water at 70° into water vapor at 160° F. The first is obviously (12,000) (0.84) (0.18) (240−70) or 309,000 B.t.u. per hr. and the second 1092 B.t.u./lb. of water, and for 1920 lbs. of water, 2,098,000 B.t.u. per hr., making 2,407,000 B.t.u. per hr. in all. This heat is furnished by the cooling of the flue gases from 1065° F. to 160° F. As shown by Fig. 5, p. 14, each 100 lb. mols of dry flue gas entering the drier contain 3.2 lb. mols of CO_2 (giving up 9540 B.t.u. per lb. mol), 96.8 lb. mols of O_2 and N_2 (giving up 6460 B.t.u. per lb. mol), and

$$\left(\frac{22.8}{760-22.8}\right)100 = 3.09 \text{ mols of water vapor}$$

(giving up 7580 B.t.u. per lb. mol.), a total of 680,000 B.t.u. per 100 mols dry gas. Neglecting radiation loss, this therefore requires

$$\frac{2{,}407{,}000\ (100)}{680{,}000} = 354 \text{ lb. mols of dry flue gas per hour}$$

or 365 lb. mols of wet flue gas. The evaporation is 106.6 mols of water per hour, making a total of 472 mols of gas per hour leaving the drier at 160° F., or 213,500 cu. ft. per hr. giving a velocity of 4.66 ft. per sec.

In order to use these data in the design of similar apparatus, the heat transfer must be estimated. Base this figure on the unknown but relatively constant surface area (A) of charge exposed in the present drier. Evaporation may be assumed to take place at 200° F. On this assumption, the heat transfer takes place in three stages: first,

$$(130)\ (1)\ (1920) + (130)\ (0.18)\ (10{,}080) = 480{,}000 \text{ B.t.u.},$$

are needed to raise the 12,000 lbs. of wet ore from 70° to 200°, second,

$$(1920)\ (974) = 1{,}870{,}000 \text{ B.t.u.}$$

disappear in the evaporation of 1920 lbs. of water at 200°; finally

$$(10{,}080)\ (40)\ (0.18) = 72{,}600 \text{ B.t.u.}$$

are used to superheat the ore from 200 to 240°. Neglecting the changes of specific heats of the components of the flue gases with temperature, the gases used (354 lb. mols gas) lose (3.54) (680,000/905) = 2660 B.t.u. per degree fall in temperature. In the last stage therefore, they drop only 72,600/2660 = 27.3° to 1038° F. The drop in the second stage is not so directly estimated because the gases are cooled not only by the evaporation of the water, but also by the dilution with the water vapor produced. Call the gas temperature at the end of the second stage t ° F. Then from a heat balance in the evaporating zone, $2660\ (1{,}038 - t) = 1{,}870{,}000 + 1920\ (0.48)\ (t - 200)$ whence $t = 300°$ F.

	Hot End	End of Evaporation	Start of Evaporation	Cold End
Temperature of gases...	1065	1038	. 300	160
Temperature of charge..	240	200	200	70
Temperature difference..	825	838	100	90
Average Δt for each stage of process.....		832	347 *	95

* The log mean, though not strictly applicable to this case on account of the dilution effect, is used as an approximation.

For each section of the drier corresponding to each of the three stages of the process one may write [1]

$$\frac{Q/\theta}{(\Delta t_{av})} = hA,$$

where the subscript 1; 2; 3 corresponds to the first; second; third stage of the drying operation. Obviously, the total exposed area in the drier,

$$A = A_1 + A_2 + A_3.$$

For each section Q/θ and Δt_{av} are given; hence,

For superheating zone, $hA_1 = \dfrac{Q_1/\theta}{(\Delta t_{av})_1} = \dfrac{72{,}600}{832} = 87$ B.t.u./hr. per ° F.

[1] For nomenclature, see pp. 178 to 179.

For evaporating zone, $hA_2 = \dfrac{Q_2/\theta}{(\Delta t_{av})_2} = \dfrac{1{,}870{,}000}{347} = 5390.$

For preheating zone, $hA_3 = \dfrac{Q_3/\theta}{(\Delta t_{av})_3} = \dfrac{486{,}000}{95} = 5120.$

The main resistance to the flow of heat in all three zones is that of the gas film. This coefficient (h) varies as the mass velocity of the gases, which velocity is practically constant for this problem. Adding,

$$hA_1 + hA_2 + hA_3 = 10{,}600.$$

The mols of air to be used in the cooler are found by using the nitrogen content of the flue gas, since this came from the air, *i.e.*,

$$\text{mols of air} = 354\ \frac{79.5}{79.1} = 356.$$

The heat to be recovered in the cooler is 85 per cent of 309,000 B.t.u. or 738 B.t.u./mol of air heated. Since one mol of air at 70° has a heat content (above 32° F.) of 243 B.t.u., at its point of exit from the cooler it will have 738 more, or a total of 981 B.t.u., corresponding to 176° F. as read from Fig. 5, p. 14.

	° F.	Difference
Temperature of air entering cooler.....	70	25.5
Temperature of ore leaving cooler *.....	95.5	
Temperature of ore entering cooler.....	240	64
Temperature of air leaving cooler.....	176	
Hence log. mean temperature difference = ...	.....	41.8° F.

* Ore cooled 85 per cent of (240 − 70).

The value of hA for the cooler is therefore determined by the equation

$$hA = \frac{Q/\theta}{(\Delta t_{av})} = \frac{(0.85)\ (309{,}000)}{(41.8)} = 6290.$$

Since the original drier gave a total value of hA of 10,600, and since the value of this quantity is obviously proportional to the volume of the drier, the cooler should be $\dfrac{6290}{10{,}600}$ the size of the drier, or 60 per cent. To keep the air velocity practically the same, the diameter should be the same, but the cylinder six-tenths the length.

This drier gives trouble in operation, in that the temperature of the discharging material fluctuates widely. When the rate of feed decreases slightly,

the discharge is exceedingly hot; with an increased rate of feed, the material is incompletely dried. The difficulty lies in the fact that the superheating zone, after evaporation is completed, is too short, and the gas temperature at that point too high. To secure a larger factor of safety in operation, the superheating zone should be longer and the gas temperature lower. This can be accomplished by resort to the "double pass" principle. (See p. 500.)

3. Design of Air Driers for Sensitive Materials

Introduction.—It should be noted that the basic differential drying equation applies only under definite drying conditions. In any continuous drier, drying conditions may vary from point to point in the apparatus, but since they remain constant at any given point Eq. (5) applies at each such point. It must therefore be applied differentially and integrated for the drier as a whole.

For the general case, *i.e.*, where both surface evaporation and interior diffusion should be taken into account, integration is complicated. Usually satisfactory approximate equations may be developed.

Where interior diffusion is controlling it is usually allowable to neglect variation in α in a given drier and Eq. (11) may be integrated directly, giving Eqs. (12), (13) and (19).

Where surface evaporation is the controlling factor the important variable is the humidity, and Eq. (6) can be integrated as shown below. Discussion is therefore limited to modifications of Eq. (6). For continuous apparatus where surface evaporation is controlling the *general* differential equations applicable to driers of adiabatic, constant temperature, or controlled humidity type will be derived. Two such equations must be established, one for counter-current flow of air, and the other for parallel flow. These equations will then be integrated for the special cases given. Finally, a discussion of intermittent driers will be added.

In any drier in which the stock is dried by means of air, and where surface evaporation is the controlling factor, the differential equation, as shown on page 517, is:

$$-\frac{d(T-E)}{(T-E)}=\frac{2\beta d\theta}{L}=\frac{2\,[f(v)]\,(p_s-p)\,d\theta}{L}, \quad . \quad . \quad . \quad (6)$$

where, at any time θ, T is the *total* water on the dry basis, E is the *equilibrium* water on the dry basis, L is the thickness of the stock, β is the experimentally determined coefficient of surface

evaporation for the definite drying conditions and particular material. As indicated by the equation, $\beta=f\,(v)\,(p_s-p)$, where v is the mass velocity of the air past the stock, and p_s-p is the partial pressure gradient of water vapor through the air film on the stock. It is convenient to substitute (H_s-H) for (p_s-p), where H_s is the humidity of the inner face of the air film on the surface of the sheet, and H is the humidity of the drying air. The change in units is obviously taken care of by the term b, the experimentally determined constant in the surface evaporation coefficient,

$$\beta=\frac{bf\,(v)\,(H_s-H)}{2}.$$

It is convenient to replace the term for free water $(T-E)$ in Eq. (6) by the term W, the lbs. *free* water per lb. of bone dry stock. Making these changes Eq. (6) becomes:

$$-\frac{dW}{W}=\frac{b[f\,(v)](H_s-H)\,d\theta}{L}. \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

General Equation for Counterflow Air Driers in which Surface Evaporation is Controlling Factor

Since driers are usually designed to give constant mass velocity of the gases, the term $bf(v)$ remains constant throughout the drier. In order to allow for the variation in the humidity (H) of the air passing through the drier, one may make a moisture balance between the water lost by the stock and that picked up by the air. The subscript 0 will be used to designate the condition of *both* air and stock at the end where the stock enters, and the lbs. of free water per lb. of bone dry stock and the humidity of the air, will be called W and H respectively at any section x feet distant from the feed end and W_1 and H_1 respectively at the discharge end. The moisture balance between the feed end and any section x feet distant gives:

$$W_0-W=r\,(H_0-H),$$

or

$$H=H_0-\frac{W_0-W}{r},$$

where r represents the pounds of dry air per lb. of bone dry stock. It should be noted that this moisture balance is based on the

assumption of constant equilibrium moisture of the stock passing through the drier. Then, at any point in the drier, the humidity gradient, or humidity driving force, ΔH equals

$$H_s - H = H_s - H_0 + \frac{(W_0 - W)}{r},$$

or

$$H_s - H = \frac{1}{r}[r\,(H_s - H_0) + W_0 - W]. \quad . \quad . \quad (20)$$

By combining Eqs. (20) and (6*a*), one obtains the *general* differential expression for driers of this type:

$$-\frac{dW}{d\theta} = \frac{b[f\,(v)]}{Lr}[r\,(H_s - H_0) + W_0 - W]\,(W). \quad . \quad . \quad (21)$$

General Equation for Parallel Flow Air Driers in which Surface Evaporation is Controlling Factor

Calling the lbs. of water per lb. of dry stock at the feed end W_0 and the humidity of the air entering at the same end H_0, a moisture balance[1] gives

$$(W_0 - W) = r\,(H - H_0),$$

or

$$H = H_0 + \frac{W_0 - W}{r}.$$

Hence the humidity gradient (ΔH) at any point in the drier equals

$$H_s - H = \frac{1}{r}[r\,(H_s - H_0) - W_0 + W]. \quad . \quad . \quad . \quad . \quad (22)$$

By combining Eqs. (6*a*) and (22) one obtains the *general* differential equation for driers of this type:

$$-\frac{dW}{d\theta} = \frac{b[f\,(v)]}{Lr}\,[r\,(H_s - H_0) - W_0 + W]\,(W). \quad . \quad . \quad (23)$$

The general equations (21 and 23) just derived apply to all counter-current and parallel flow driers respectively which operate at temperatures so low that the rate of surface evaporation is the controlling factor, *however the heat be applied to the driers.* To integrate them, however, the exact method of heat supply must be taken into account.

[1] This equation also assumes E to be constant.

Equation for Adiabatic Driers; Counter-Current Flow; Surface Evaporation Controlling; No Shrinkage

The salient characteristic of adiabatic driers is constancy of wet bulb temperature, *i.e.*, $t_s = t_w$, and consequently $H_s = H_w$.[1] These driers are therefore used for materials sensitive to heat while still wet, as the stock temperature is automatically controlled (*e.g.*, glue, sugar, heavy leather, vegetables, etc.)

Since in any given drier of this type, H_w, H_0 and W_0 are constant, Eq. (21) may be written as

$$-\frac{dW}{(W)\,(M - W)} = \frac{bf\,(v)\,d\theta}{Lr},$$

in which

$$M = r\,(H_w - H_0) + W_0. \quad . \quad . \quad . \quad (24)$$

Using the subscripts 0 and 1 to designate the condition of both air and stock at the feed and discharge ends, respectively, integration gives:

$$ln_e\left(\frac{(W_0)\,(M - W_1)}{(W_1)\,(M - W_0)}\right) = \frac{b[f\,(v)]\,M\theta}{Lr}, \quad . \quad . \quad . \quad (25)$$

where M is defined by Eq. (24).

If the total weight of dry stock exposed in the drier be called R', and the weight of dry stock fed per unit time be called R, it is obvious that

$$\frac{R'}{R} = \theta,$$

where θ is the drying time. For example, Eq. (25) may be written as

$$ln_e\left(\frac{(W_0)\,(M - W_1)}{(W_1)\,(M - W_0)}\right) = \frac{b[f\,(v)]\,MR'}{LrR}. \quad . \quad . \quad . \quad (25a)$$

This type of drier, simple in construction and operation, can be used to control the humidity and temperature of the air with which the dried stock is in contact, and hence to control the moisture content of the product (*e.g.*, water of crystallization, textile products, etc.) and yet simultaneously secure rapid evaporation due to the high initial temperature of the drying air.

Illustration 2. (Adiabatic Counterflow Drier.)—It is desired to design a continuous, *counter-current*, adiabatic, rotary drier to produce 500 lbs. per hour of product containing 2 per cent moisture (wet basis), from a wet crystal

[1] The assumption that $H_s = H_w$ is made to obtain an approximate solution (see Fig. 101, p. 417).

mass containing 50 per cent moisture (wet basis), using air with a humidity of 0.010, heated to a temperature of 250° F. The air is to be cooled to 60 per cent humidity. To avoid blowing the material out of the drier, the air velocity must not exceed that in the experimental runs,[1] *i.e.*, 10.2 lbs./sq. ft./min. The charge per unit volume shall also equal that in the experimental runs, 5.1 lbs. of wet charge, or 2.55 lbs. of dry per cu. ft. $bf(v)/L=0.70$.

Solution.—First determine the dry material and water per hr. The product, 500 lbs. is 2 per cent water, or 490 lbs. of dry and 10 lbs. of water. The entering water is equal to the dry material, or 490 lbs. The evaporation is the difference, or 480 lbs. Hence $W_0=1.0$, $W_1=0.0204$, and $R=8.17$ lbs. of bone dry stock per min. Next, determine the necessary air consumption. Air at a condition of $t=250$, $H_1=0.010$, cooling adiabatically to 60 per cent humidity falls to $H_0=0.0411$, H_w being 0.0142 (see Fig. 102, p. 443). The humidity increase is, therefore, 0.0311, or $u=(8/0.0311)=257$ lbs. dry air/min. The allowable air velocity being 10.2 lbs./sq. ft./min., this requires a drier cross-section of 25.2 sq. ft. The equation for this case connecting the drying capacity and size is given as Eq. (25*a*):

$$ln_e\left(\frac{W_0(M-W_1)}{W_1(M-W_0)}\right)=\frac{bf(v)MR'}{rRL},$$

where

$$M=r\,(H_w-H_0)+W_0.$$

From the experimental runs $bf(v)/L$ was found to be 0.70. Inserting these values in this equation, R' is found to be 2102 lbs. of dry stock. The drier volume must therefore be $2102/2.55=824$ cu. ft. Since the section is 25.2 sq. ft., the length must be about 33 ft. The material is in the drier a time $\theta=R'/R=257$ mins. To provide a reasonable factor of safety in capacity, a drier no less than 6 ft. diameter by 40 or 50 ft. should be used.

If the charge is fed to this drier below about 100° F. (the wet bulb temperature) its length must be slightly increased to provide for preheating the charge up to this point.

Illustration 3. (Adiabatic Counterflow Drier for Sheet Material.)—Let it be required to design a counter-current, adiabatic wire-shelf drier for a certain fibre-board, conforming to the following conditions:

Initial air temperature shall not exceed 120° F.; $H=0.0053$.
Initial water content of wet board, 70 per cent free water, wet basis.
Final water content of dry board, 10 per cent free water, wet basis.
Initial wet sheets, 30 in. by 42 in. by $\frac{15}{48}$ in., weighing 15.9 lbs. each.
Maximum air velocity parallel to sheets, 4 ft. per sec.
Humidity of exit air, 70 per cent.
Capacity, 1000 lbs. product per hour.
Net space between shelves, 1 in.
Material does not shrink appreciably on drying, and

$$ln_e\frac{W_0}{W}=\frac{bf(v)(H_w-H)\theta}{L},$$

[1] See pp. 552 to 554.

where

$$bf(v)=0.277v/(v+3.07).$$

L is the wet thickness in inches, θ is the drying time in minutes, and v is the air velocity in ft. per sec. at 120° F. and 1 atm. parallel to the sides of the sheets, the material being placed on shelves of chicken wire and *dried from both sides.*

Solution.—The hourly evaporation is 2000 lbs. From the humidity chart, the wet bulb humidity, H_w, is 0.0162, while the humidity of the air leaving the drier, H_0, is 0.0148. The water picked up per 100 lbs. of air is therefore $100\,(0.0148-0.0053)=0.95$, whence the hourly air requirement is 211,000 lbs. ($u=3520$ lbs. bone dry air per min.). Since a linear velocity of 4 ft. per sec. corresponds to 980 lbs. per sq. ft. per hr., the net cross-section available for air must be 215 sq. ft., and the gross cross-section to allow for stock must be $(1+\frac{15}{48})$ times as much, or 282 sq. ft. Since the humid volume at 120° F. is 14.7 cu. ft. per lb. of bone dry air, the volume of entering air equals

$$(3520)\,(14.7)=51{,}800 \text{ cu. ft. per min. at } 120° \text{ F.}$$

The drying equation for an adiabatic counterflow air drier is as follows:

$$ln_e\left(\frac{(W_0)(M-W_1)}{(W_1)(M-W_0)}\right)=\frac{bf(v)MR'}{LrR}. \quad . \quad . \quad . \quad . \quad . \quad (25a)$$

Since the pounds of bone dry stock per hour equals 900, $r=234$ lbs. of bone dry air per lb. of bone dry stock, $W_0=(70/30)$ or 2.33, $W_1=(10/90)$ or 0.111, and $M=r(H_w-H_0)+W_0=234\,(0.0162-0.0148)+2.33=0.328+2.33=2.66$. Hence the left-hand member of Eq. (25*a*) equals

$$2.3\log_{10}\frac{(2.33)\,(2.66-0.11)}{(0.111)\,(0.328)}=5.08.$$

Since $R=(900/60)=15$ lbs. of bone dry stock per minute, $L=\frac{15}{48}=0.313$ in., and $bf(v)=0.277\,(4/7.07)=0.157$, the right-hand side of Eq. (25*a*) is:

$$\frac{(0.157)\,(2.66)\,(R')}{(0.313)\,(234)\,(15)},$$

whence R' equals 13,350 lbs. of bone dry stock in the drier at any time, or the time of drying equals (R'/R) or *891 min.* Since each wet sheet weighs 15.9 lbs. when containing 70 per cent water on the wet basis, each sheet contains $(15.9)\,(0.3)=4.77$ lbs. of bone dry stock. Hence the total number of sheets in the drier is $(13{,}350/4.77)=2800$. It would be best to place the long side of the sheets across the drier, thus having shelves $3\frac{1}{2}$ ft. wide. To provide 282 sq. ft. of section one may employ seven tunnel driers each 7 ft. wide net, thus providing for $3\frac{1}{2}$ ft. shelves removable from opposite sides of each drier, the shelf space being about 5 ft. 9 in. or 52 sheets high. A section of the drier perpendicular to its length cuts, therefore, 728 sheets. Hence the drier is 2800/728 or 3.85 sheets long. Since in this direction each sheet is $2\frac{1}{2}$ ft., this requires a drier slightly less than 10 ft. long. To provide a reason-

able factor of safety, the drier must be built not less than 12½ ft., preferably 15 or even 17½ ft. long. Note that the oversize is distributed entirely lengthwise the drier; otherwise the air velocity would be reduced with a consequent loss in evaporation rate which at low air velocities would render much less effective an increase in size due to increase in cross-section.

Equation for Adiabatic Driers; Parallel Flow; Surface Evaporation Controlling; No Shrinkage

Since in any given drier of this type r, H_w, H_0 and W_0 are constant, Eq. (23) may be written as

$$-\frac{dW}{(W)\ (N+W)}=\frac{b[f(v)]\ d\theta}{Lr}$$

in which

$$N=r\ (H_w-H_0)-W_0. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Using the subscripts 0 and 1 to designate the feed and discharge ends, respectively, integration gives:

$$ln_e\left(\frac{(W_0)\ (N+W_1)}{(W_1)\ (N+W_0)}\right)=\frac{b[f(v)]\ N\theta}{Lr}=\frac{b[f\ (v)]NR'}{LrR}, \quad . \quad (27)$$

N being defined by Eq. (26).

Illustration 4. (Adiabatic Parallel Flow Drier.)—If the material of Illustration 2 be dried adiabatically in the same sort of apparatus, with the same initial drying conditions, *but with parallel flow of air*, the quantity of air, and hence the final humidity, both remaining unchanged, the quantity, N, is found by substitution of these values to be 0.075; and from Eq. (27):

$$ln_e\left[\frac{(W_0)}{(W_1)}\ \frac{(N+W_1)}{(N+W_0)}\right]=\frac{bf(v)N\theta}{Lr},$$

$\theta=866$ minutes drying time requiring a correspondingly larger drier, *as compared with* 257 *mins. for counter-current flow.*

The reason for this three-fold greater drying time and size of drier lies in the fact that counter-current flow maintains a high value of ΔH throughout the dry end of the apparatus, thus securing a relatively rapid drying rate in this zone, whereas parallel flow loads the air with moisture before it comes in contact with the nearly dry material, thus involving a low drying rate as the material nears dryness.

Equation for Constant Temperature Driers; Counter-Current Flow; Surface Evaporation Controlling; No Shrinkage

Materials injured by heat after they have become dry are usually dried in constant temperature driers. This is necessary in the case of materials existing in large lumps or thick sheets

(for example, raw rubber), because when the drying operation is even partially complete, the surface of the sheet or lump is relatively dry, the remaining moisture existing only in the interior. While the interior is therefore cold, the surface is practically at the temperature of the drying air and therefore liable to injury. In present commercial practice, these driers are also frequently used for materials such as salts with water of crystallization, textiles, and the like, which, as will be shown later, are more advantageously handled in other apparatus.

The drying capacity of any drier in which the air temperature is kept up to a constant level by supplying heat in the necessary quantity in the drying compartment itself, is found by the use of the integral of the general equation for surface evaporation only and negligible shrinkage.

$$-\int_{W_0}^{W_1}\frac{dW}{(W)\ (\Delta H)}=\frac{b[f\ (v)]\theta}{L}=\frac{b[f\ (v)]\ R'}{LR}. \quad . \quad . \quad . \quad (28)$$

This integral involves, however, not one but two variables, W and ΔH, and, unlike the case of adiabatic driers, it is impracticable to express ΔH algebraically in terms of W. None the less ΔH can be found as follows. For various values of W, between W_0 and W_1, calculate H from $H=H_0-\frac{(W_0-W)}{r}$. Knowing the operating temperature, t, and the humidity, H, just calculated, H_w can be read directly from the humidity chart. ΔH is H_w minus H. Knowing ΔH for various values of W, it is possible to plot $1/(W)\ (\Delta H)$ against W, and the area under this curve is the integral required.

Illustration 5. (Constant Temperature Counterflow Drier for Sheet Material.)—Design a constant temperature counter-current drier for the fibre board of Illustration 3, other conditions remaining unchanged.

Solution.—From the humidity chart, air leaving at 70 per cent saturation at 120° F. has a humidity H_0 of 0.0562, and, since the air entered at $H_1=0.0053$, it picks up 0.0509 lb. water per lb. of dry air. To evaporate 2000 lbs. of water hourly requires therefore 655 lbs. of air per minute (u). Since the air velocity is 980 lbs. per sq. ft. per hr. (see Illustration 3) the net sectional area is about 40 sq. ft., and the gross cross-section is $(1+\frac{1}{4}\frac{5}{8})$ times as much, or 52.5 sq. ft. As before $W_0=2.33$, $W=0.111$, $R=15$ lbs. of bone dry stock per minute, and $r=(655/15)=43.7$ lbs. bone dry air per lb. of bone dry stock, but R' must be calculated by graphical integration of the equation,

$$\int_{W_1}^{W_0}\frac{dW}{W\Delta H}=\frac{bf(v)R'}{RL} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The variables, W and H, are connected by the water balance equation,

$$H = H_0 - \frac{(W_0 - W)}{r} = 0.0562 - \frac{(2.33 - W)}{43.7}.$$

From this latter equation the values of W between the initial and final values of H have been calculated for several assumed values of W between the initial and final values of 2.33 and 0.111 lbs. water per lb. bone dry stock. With these values of H the values of H_w have been read from the humidity chart. The difference between these two figures is ΔH, and from this $1/W\Delta H$ can immediately be obtained. The tabulated steps for the calculation of four typical points follows:

W	H	H_w	$\Delta H = H_w - H$	$1/W\Delta H$
0.111	0.0053	0.0162	0.0109	826
0.462	0.0134	0.0225	0.0091	238
0.933	0.0241	0.0310	0.0069	155.5
2.33	0.0562	0.0585	0.0023	186.5

The last column ($1/W\Delta H$) plotted against W is shown in Fig. 129; the value of the area under this curve is found by planimeter to be 8.64 squares, and allowing for the scale of the plot, 50 units per square, $\int_{W_1}^{W_0} \frac{dW}{W\Delta H} = 432$. By substitution in Eq. (30), $R' = 12{,}900$ lbs. bone dry stock in the drier, *i.e.*, fortuitously the drier is of almost exactly the same size as before, but the cross-section is about one-fifth as great, the drier being longer to correspond. Three driers, each $3\frac{1}{2}$ ft. wide by 5 ft. $\frac{3}{8}$ in. high will serve. The theoretical length is about 48 ft. A length of 75 or 80 ft. would allow a suitable factor of safety in operation. Note that much less air is required for this drier at constant temperature than when operated adiabatically. If the same amount of air were used in both cases, the constant temperature drier would be smaller in volume than the adiabatic drier.

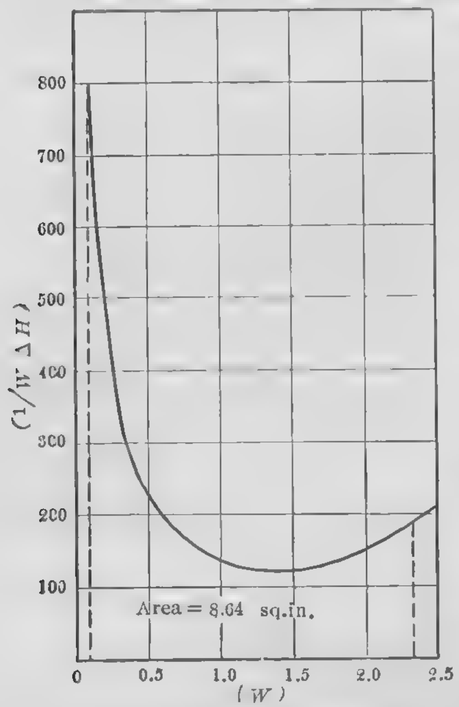


FIG. 129—Graphical Integration of $dW/W(\Delta H)$.

When the air temperature is high (above 200° F.) the value of ΔH usually changes but little during the drying operation. In such a case an average value, $(\Delta H)_{av} = \frac{(\Delta H)_0 + (\Delta H)_1}{2}$, may be used, and the equation becomes, where shrinkage is negligible:

$$ln_e \frac{W_0}{W_1} = \frac{b[f(v)]\, R'\, (\Delta H)_{av}}{LR}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Illustration 6. (Constant Temperature Counterflow Drier.)—How much smaller could the drier of Illustration 2 be made if the air temperature could be maintained constant throughout its entire length at 250°, using, however, the same amount of air, each pound therefore picking up the same amount of moisture as before?

The initial value of ΔH is, as before, 0.0345. The final value of ΔH as read from the chart for air at 250°, with $H = 0.0411$, is $0.0738 - 0.0411 = 0.0327$. The mean value of ΔH is 0.0336. The equation used to determine capacity for a counterflow constant temperature drier is given as Eq. (29):

$$ln_e \frac{W_0}{W} = \frac{bf(v)R'(\Delta H)_{av}}{LR},$$

whence by substitution of values, $R' = 1350$ lbs. dry stock; the drier volume is 530 cu. ft.; the theoretical length is 21 ft. as compared with 33 ft. required for an adiabatic drier.

This drier could be made to operate at substantially constant temperature by supplying it with steam heating pipes along its length.

Equation for Constant Temperature Driers; Parallel Flow; Surface Evaporation Controlling; No Shrinkage

As in the preceding case, the equation is,

$$-\int_{W_0}^{W_1} \frac{dW}{(W)\,(\Delta H)} = \frac{bf\,(v)\,\theta}{L} = \frac{b[f\,(v)]\,R'}{LR}, \quad . \quad . \quad . \quad (30)$$

which must be evaluated by graphical integration. The difference from the preceding case lies in the fact that H, to be used in calculating ΔH, must be obtained from the expression,

$$H = H_0 + \frac{(W_0 - W)}{r}.$$

Controlled Humidity Driers.—Crystals containing water of crystallization must be dried without efflorescence because once the crystal water is lost, even in part, the form of the crystal is destroyed and the water recovered very slowly. Certain materials containing adsorbed water deteriorate permanently if that water

be removed beyond a certain point (*e.g.*, soda-lime for gas absorption). Finally certain materials must be dried to avoid injury (*e.g.*, paper, etc.). In all these cases there exist definite limits of humidity and temperature which must not be exceeded in the drying process, *i.e.*, humidity must be controlled. The mechanisms for securing this control are described on p. 506. The equations for the design of such driers are identical with those used for constant temperature driers, the one difference being

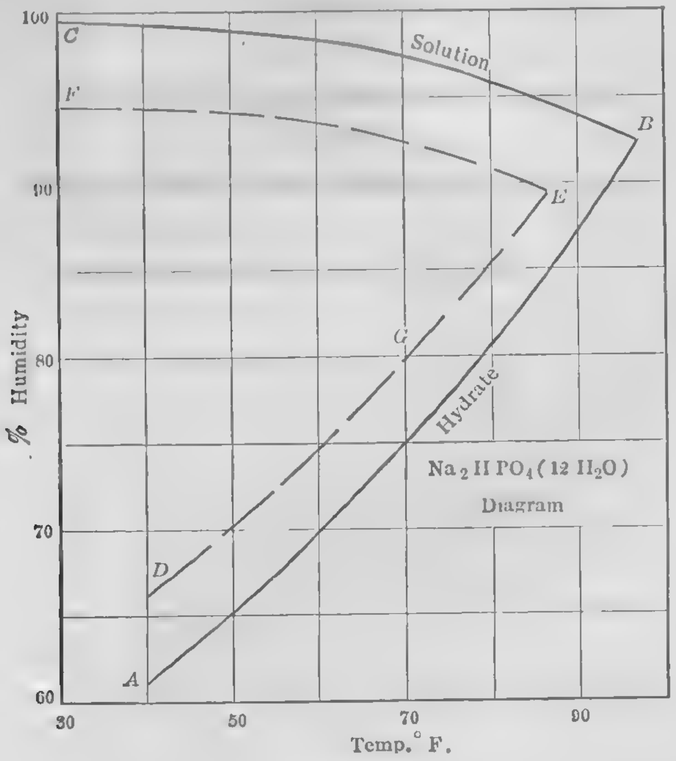


FIG. 130.

that one must use the temperature corresponding to each value of the humidity limitations of the particular material being dried.

Illustration 7. Controlled Humidity Drier. (Counterflow Drying of Crystals.)—The determination of the humidity limits which must be observed will be clear from the following illustration:

Crystals of $Na_2HPO_4.12H_2O$ lose water of crystallization if subjected to conditions of temperature and humidity corresponding to any point *below* AB[1] in Fig. 130. The same crystals will deliquesce, *i.e.*, dissolve to form a solution,

[1] For the construction of these curves see pp. 556 to 557.

at any condition *above* the line CB. Therefore, drying conditions must be so chosen that the drying air will at all times be represented by some point in the field ABC. In practice it will be necessary to design the drier to operate above AB, along some such line as DE, chosen to secure a satisfactory *factor of safety* against efflorescence, and below the line EF, this latter being sufficiently low to maintain a reasonable evaporative rate. Furthermore, the crystals must be cooled and stored prior to packing, in air the humidity of which lies in the same field. It is obvious from the plot that the temperature of the crystals leaving the drying zone theoretically must not exceed 97° and for safety should be below 86°. This latter temperature gives, however, a humidity difference and hence a drying rate so low that it is agreed not to allow the air to rise above 85 per cent humidity. Therefore it must not rise above 79°. If, for example, air at 70° F. and of 80 per cent humidity is to be used, design the drier to operate with a counter-current stream of air, entering at the point G, and rising in temperature as its humidity increases along the curve GE, the air being discharged at 79° F. with a humidity of 85 per cent. In this way one will at all times maintain the highest drying temperature and evaporative rate consistent with safety.

Assume that it be required to produce hourly 200 lbs. of crystals of apparent specific gravity 0.9, containing not over 0.5 per cent moisture (wet basis) from wet crystals carrying 5 per cent of free water, wet basis. In the drier the crystals rest in a layer 1 in. deep in perforated trays set to give 1 in. clear space between the trays. Between these trays air passes at a rate of 25 lbs. per square foot of clear cross-section per minute. For the sake of illustration, assume that under these conditions experiments show that a drying coefficient, $bf(v)/L$, equal to 3.0[1] can be realized and that the material contains no "equilibrium moisture."

Solution.—Two hundred pounds of product containing 0.5 per cent moisture corresponds to an hourly evaporation of 9.48 lbs. of water. R equals 3.32 lbs. of dry stock per min. The air enters the drier with a humidity of 0.0125 and leaves with a humidity of 0.0188; hence each 100 lbs. of air pick up 0.63 lbs. of water, requiring for the above amount 1505 lbs. of air per hour, or 25.1 lbs. per min. The net cross-section of the drier is therefore 1 sq. ft., and the gross cross-section is 2 sq. ft., neglecting the thickness of the trays.

The length of the drier depends upon the number of pounds of dry stock, R', which must be in it at any time to produce 200 lbs. of product per hour. This quantity is given by Eq. (29):

$$ln_e\frac{W_0}{W_1}=\frac{bf(v)(\Delta H)_{av}R'}{LR},$$

provided (ΔH) varies only slightly throughout the drier.

The water on the wet crystals exists as a saturated solution and during drying will not be at the wet bulb temperature, but owing to vapor pressure lowering, at a somewhat higher temperature than this, with a percentage

[1] $\frac{bf(v)}{L}=3.0$, when using time in minutes and ΔH as in this illustration. See Eq. (29) p. 545.

humidity of about 98. From the humidity chart it will be seen that air entering the drier at 70° F. and $H=0.0125$ has a wet bulb temperature of 66° F. and a humidity at the wet bulb temperature of 0.01345. By interpolation on the cooling line the value of H is 0.01336, giving ΔH or H_s-H equal to 0.00086. Similarly at 75° ΔH equals 0.00077, and at 80°, 0.00062. The change in value of ΔH with temperature is therefore not so great but that an average value (ΔH_{av}) of 0.00075 may be employed in the above equation.

By substitution R' (dry basis) is found [1] to be 3465 lbs., corresponding to about 3480 lbs. product in the drier at any time. This product weighs

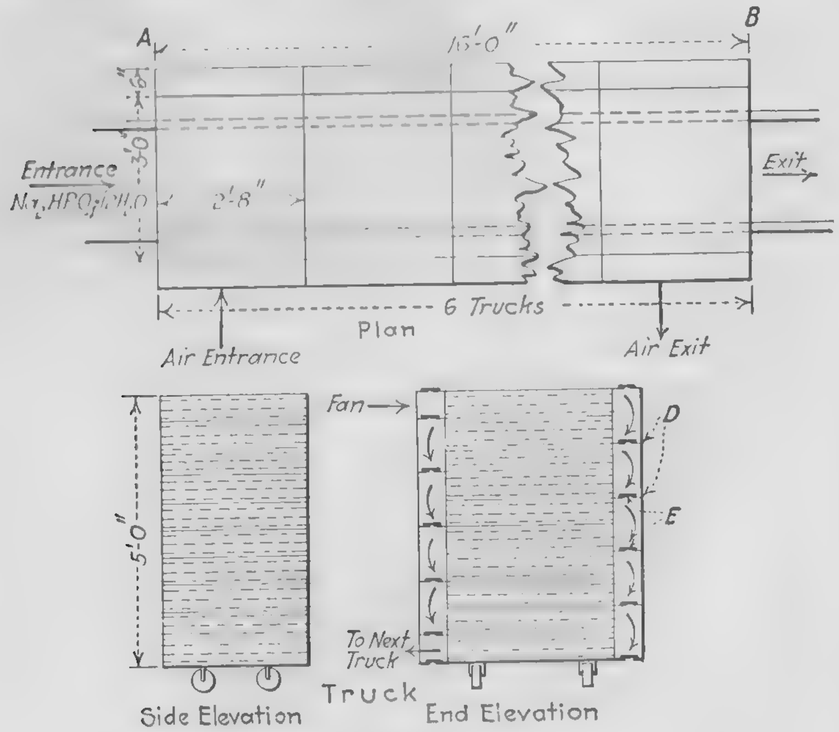


FIG. 131.

56.1 lbs. per cu. ft. and has a volume therefore of 62.1 cu. ft. Since the net cross-section of crystals is 1 sq. ft., the length of the drier must be 62.1 ft.

Such a drier provides for sufficient air at the proper velocity flowing counter current to the stock; its dimensions are, however, impractical. The same conditions may be maintained by constructing the drier as shown in Fig. 131. If trucks 5 ft. high, 3 ft. wide and 2 ft. 8 ins. long are used, each truck will contain thirty shelves. Each truck will then hold

$$(30)\ (3)\ (2.67)\ (1/12)=20 \text{ cu. ft. of crystals,}$$

[1] $2.3 \log_{10}\left(\frac{(0.05/0.95)}{(0.005/0.995)}\right)=\frac{(3.0)\ (0.00075)\ (R')}{3.32}$, whence $R'=3465$.

hence about three trucks are needed to hold 62 cu. ft. of crystals. In order to provide a suitable factor of safety, six trucks should be used.

The enclosure AB is the tunnel with inside dimensions about 5 ft. high by 4 ft. wide by about 16 ft. long. Through this space are propelled six trucks, each supporting thirty shelves. The air has in addition to its motion counter to the trucks a rapid transverse circulation across the trucks as indicated by arrows. This transverse movement is reversed in successive compartments to secure uniformity in drying. Short-circuiting of the air is prevented by the horizontal partitions D, leather flaps E being used as seals at the lines of contact. Heating elements must be provided in the sides of the drier, so controlled as to maintain the required temperature-humidity relations at each point.

Intermittent Adiabatic Driers

Occasion may arise for the use of an intermittent adiabatic drier, *i.e.*, the drier being filled with charge, and then run until the drying process is completed, when it is emptied to give way to a new charge. Such an arrangement is always to be avoided, if possible, as it involves *first*, slow drying toward the end of the cycle, with consequent low drying efficiency, *i.e.*, poor utilization of the heat content of the air, and *second*, unequal drying due to the rapid drying of the stock at the point where the fresh, dry, hot air enters, and slow evaporation at the other end where the cooled, moisture-laden air leaves.

This second disadvantage can in a large degree be eliminated by using either a short, rotary drier with provision for mixing the charge from end to end during the drying, or using a shelf or tray drier, and in either case periodically reversing the direction of the air current. In such an apparatus the rate of drying varies from point to point at any given time during the drying cycle, due to the rise in humidity of the air as it traverses the apparatus, and decreases as the drying proceeds, due to the influence of the continually decreasing moisture in the stock. In other words, the drying rate is a function of two independent variables, *i.e.*, of the time in the drying cycle, and of the location of the stock in the drying apparatus with reference to the points of entrance and exit of the air. These conditions, however, obtain in the small scale experiments which are necessary to establish, for any given materials, the constants required for the design of a drier. The consideration involves the solution of a partial differential equation.

Derivation of Equation.—For such a case, *i.e.*, where the charge is kept thoroughly mixed, let z = the actual total water content in the drier at any time, θ, from the beginning of the run; w = the concentration of water in the stock; a = the surface area of the stock, available for evaporation, per unit volume of the drying equipment; . S = the cross-section of the apparatus; x = the distance of any specific point in the apparatus from the end at which the air leaves; Δz [1] = the water content of the differential length of drier, Δx; H = the humidity of the drying air at the point x in the drier, and H_w that corresponding to the wet bulb temperature; u = the weight of dry air passing through the drier per unit time.

The differential equation expressing the drying mechanism is,

$$-\frac{d(\Delta z)}{d\theta}=\left[\frac{bf(v)}{L}\right][(w)(a)(S)(\Delta x)(L)]\ [(H_w-H)].$$

Since all water evaporated goes into the air, the right-hand side of this equation, representing as it does, the water carried out of the section under consideration per unit time, must equal that picked up by the air:

$$u\Delta H=-bf(v)w(H_w-H)aS\Delta x.$$

By integration,

$$ln_e(H_w-H)=\frac{bf(v)waSx}{u}+\text{constant};$$

or if H_0 = the humidity of the air leaving the drier, at $x=0$,

$$ln_e\frac{H_w-H}{H_w-H_0}=\frac{bf(v)waSx}{u},$$

an equation which applies at any time, θ.

It is obvious from a water balance that throughout the drying period,

$$-dz=(u)(H_0-H)d\theta.$$

However, from the preceding integral,

$$\frac{H_w-H_0}{H_w-H}=\frac{H_w-H+H-H_0}{H_w-H}=1-\frac{H_0-H}{H_w-H}=e^{\frac{-bf(v)waSx}{u}}.$$

Since $\frac{w}{w_0}=\frac{z}{z_0}$, when the subscripts, 0, apply to the condition of the stock entering the drier at the time, $\theta=0$,

$$-dz=u(H_w-H)\left[1-e^{\frac{-bf(v)w_0zaSx}{uz_0}}\right]d\theta,$$

[1] The fact that H varies only with x is indicated by writing the differential coefficients of these variables as ΔH and Δx; since the moisture z varies only with θ, the differential coefficients of these variables are written as dz and $d\theta$. It should be noted this meaning of ΔH is different from that used elsewhere.

or if,

$$\frac{bf(v)w_0aSx}{uz_0}\text{ be designated by }Q,$$

$$-dz=(u)(H_w-H)[1-e^{-Qz}]d\theta,$$

or by integration,

$$\frac{z_0}{z}-1-\frac{1}{Qz}[ln(1-e^{-Qz})-ln(1-e^{-Qz_0})]=\frac{u(H_w-H)(\theta)}{(z)}. \quad . \quad . \quad (31)$$

If f be used to designate the function,

$$f=-\frac{1}{Qz}[ln(1-e^{-Qz})],\quad\text{and}\quad f_0=-\frac{1}{Qz_0}[ln(1-e^{-Qz_0})],$$

this equation may be written as,

$$f+\frac{z_0}{z}(1-f_0)-1=(u)(H_w-H)\frac{\theta}{z}=F. \quad . \quad . \quad . \quad . \quad . \quad (31a)$$

It is possible to simplify the term, $\frac{bf(v)w_0zSax}{uz_0}$ to $\frac{bf(v)z}{uL}$, since the total evaporative surface, Sax, is proportional to z_0 and inversely to L, and since w_0 can be assumed constant in a given drying problem, $bf(v)$ thus becoming the coefficient of evaporation of the material in question, hence,

$$Q=\frac{bf(v)}{uL}.$$

Equation (31a) cannot be solved directly for u or z, but can be solved for θ, the quantity most frequently sought in drier design. Its main use is in calculating the results of experimental runs (see pp. 552 to 554) in which case it is solved for Q by successive approximation, keeping in mind the facts, first, that f is in a definite function of Qz, (see Fig. 132), and second, that f_0 and f must correspond to a ratio of Qz_0 over Qz equal to z_0 over z.

In all these equations for driers which involve the basic equation for drying rate under constant drying conditions the term $f(v)$ represents the same quantity. Its absolute value will vary from material to material, and, in the case of a given material, will be less in any type of drier offering inadequate surface exposure. It should be noted that $f(v)$ is independent of the size of the drier or the scale of the drying operation.

The capacity of a drier is proportional to its size, provided, *first*, that the air supply be kept strictly proportional to the water to be evaporated; *second*, that air velocity past the material

be unchanged; *third*, that the wet material be dried from the same initial to the same final water content; *fourth*, that the average thickness or dimension of the material be constant; *fifth*, that the temperature and humidity of the initial air be kept the same; and finally, *sixth*, that the degree of exposure of the surface to the drying air be maintained. If in experimentation these conditions be fixed at the values it is desired to realize in practice then the size of a drier of exactly the same type can be figured by simple proportionality. When, however, any one of these conditions is to be different from those obtaining in the experiment,

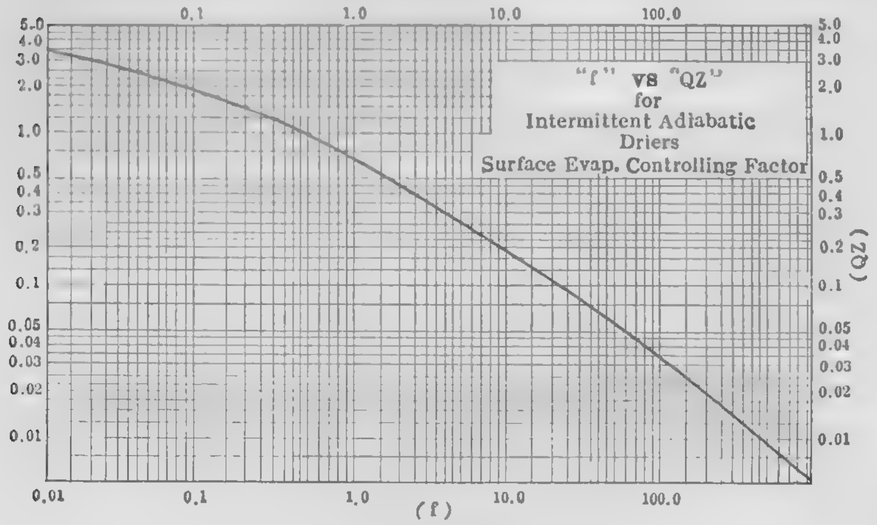


FIG. 132.

or another type of flow is to be used, proportionality no longer holds, and resort must be had to the equations.

As has already been emphasized, the constants for the design of drying apparatus must be determined by experimentation upon the material itself. In such experiments it is important to have the nature of exposure of the material to the drying air similar to that in the apparatus which it is proposed to build.

Interpretation of Laboratory Data for an Intermittent Adiabatic Drier

For example, let it be required to build a rotary drier, in which wet crystals, insoluble in water, relatively fine, but not a powder, are to be dried. The crystals carry on the average their own weight of water. In the laboratory these crystals were dried

in a small improvised experimental apparatus, consisting of a 6-in. galvanized stove pipe, 5 ft. long, to the inside of which were riveted flat 1-in. shelves of sheet metal, radially directed. It was supported on a small iron pipe, and was rotated at 30 r.p.m. The preheated air was forced through the drier by a small 6-in. fan. The drier handled several pounds of the wet crystals, and for convenience[1] was run intermittently until the charge was satisfactorily dry. The apparatus was easily constructed and operated; the log sheets of two characteristic runs are given below.

The equation for an adiabatic drier operated intermittently applies to this operation; indeed the most frequent use of this equation is in the interpretation of such small scale experimental data.

The value of Q for these runs was found by trial and error (see p. 551), using the curves of "f" vs. "Qz" (shown in Fig. 132, p. 552) in connection with Eq. (31a).

$$f+\frac{z_0}{z}(1-f_0)-1=u\,(H_w-H)\frac{\theta}{z}=F.$$

Different values of Q were tried until one was found which made the columns, $u\,(H_w-H)\frac{\theta}{z}$, and $f+\frac{z_0}{z}(1-f_0)-1$, the latter expression being designated F, as nearly equal as possible. These values may be made exactly equal for the data corresponding to any one time of operation. Theoretically they should then be equal throughout the run. Deviations at other experimental points are due to experimental error and to the fact that the theory is but an approximation. That value of Q should be chosen which makes the results as a whole most nearly concordant. After a little experience the determination of Q for a given run is a simple matter.

The average lump size of this material is unknown but approximately constant. The term L is, therefore, not separately estimated, the whole expression $bf(v)/L$, being considered as the drying coefficient.

[1] Since the interpretation of the data was rendered complex by the use of intermittent operation, it would have greatly simplified calculations if the drier had been operated continuously.

Drying Wet Crystals

Run 1. $u=2$ lbs. of bone dry air/min.
Weight of charge = 5 lbs.
Atmospheric moisture, $H=0.009$
Air temp., 260° F.; $H_w=0.046$; $u(H_w-H)=0.074$.
Initial moisture = 50.4% (wet basis)
Final moisture = 1.0% (wet basis)
$Q=0.336$; $f_0=0.66$; $bf(v)/L=0.67$

Time (Min.)	Loss in Weight	z = Water Content of Sample (Lbs.)	$0.074\frac{\theta}{z}$	F
0	....	2.52		
30	0.87	1.65	1.3	1.0
60	0.43	1.22	3.6	2.4
90	0.32	0.90	7.4	4.5
120	0.75	0.15	59.2	63.7
150	0.12	0.025	444	610

Run 2. $u=2$ lbs. of bone dry air/min.
Weight of charge = 5 lbs.
Atmospheric moisture = 0.008
Air temp., 220° F.; $H_w=0.037$; $u(H_w-H)=0.058$
Initial moisture = 32% (wet basis)
Final moisture = 3% (wet basis)
$Q=0.35$; $f_0=1.47$; $bf(v)/L=0.70$

Time (Min.)	Loss in Weight	z = Water Content of Sample (Lbs.)	$0.058\frac{\theta}{z}$	F
0	....	1.60		
30	0.62	0.98	1.77	1.87
60	0.25	0.73	4.77	3.79
90	0.37	0.36	14.5	13.7
120	0.13	0.23	30.2	27.9
150	0.13	0.10	87.0	87.5

The velocity in this drier is relatively low, but it was found impossible to operate it at higher velocity without excessive dusting.

Nomenclature [1]

English Symbols:

a = Shrinkage coefficient of stock: $L=L_0[1+a(T-E)]$.
A = Surface of either side of sheet.
b = Constant.
C = Drying coefficient.
d = Prefix, indicating differential quantity.
E = *Equilibrium* moisture, lbs. of equilibrium water per lb. of bone dry stock.
$f(v)$ = An empirical function of mass velocity of air.
H = Humidity of air, lbs. of water vapor per lb. of bone dry air.
K = Drying coefficient = k.
L = Total thickness of stock.
M = A constant = $r(H_w-H_0)+W_0$.
N = A constant = $r(H_w-H_0)-W_0$.
n = An empirical exponent in the skin effect equation.
p = Partial pressure of water vapor.
r = Weight ratio of air to stock, lbs. of bone dry air per lb. of bone dry stock.
R' = *Total* weight of bone dry stock in the drier, lbs.
R = Rate of feed or discharge of bone dry stock, lbs. per unit time.
T = *Total* moisture in stock, lbs. of total water per lb. of bone dry stock.
t = Air temperature, deg. Fahr.
u = Rate of flow of air through the drier, lbs. of bone dry air per unit time.
v = Mass velocity of air, weight per unit time per unit of cross-sectional area.
w = *Actual* concentration of free moisture, weight per unit volume of stock.
W = *Free* moisture in stock, lbs. of free water per lb. of bone dry stock = $T-E$.
x = Thickness of skin effect.
y = *Average* concentration of free moisture, weight per unit of volume of stock.
z = Distance from center-line of sheet in the direction normal to the surface.

Greek Symbols:

α = Coefficient of diffusion of liquid water through the stock.
β = Coefficient of evaporation of water from the surface of the stock, $\beta=f(v)\ (p_s-p)=bf(v)\ (H_s-H)/2$.
δ = Prefix, indicating partial differential quantity.
ΔH = Humidity driving force = H_s-H.
Δt = Temperature difference, or driving force.
θ = Time.

[1] These definitions are adhered to throughout this chapter, except in the derivation of Eq. (31*a*), see pp. 550 to 551.

Subscripts:

s refers to the condition at the *surface* of the stock.
w refers to the condition at the *wet bulb* temperature.
e refers to the *equilibrium* condition.
a refers to air.
o, in the equations for intermittent driers, refers to the conditions at the start of the drying operation. In the equations for continuous driers, *o* refers to the condition of *both* air and stock at the end of the drier where the *stock enters* the apparatus.
1, in the equations for continuous driers, refers to the condition of *both* air and stock at the end of the drier where the *stock leaves* the apparatus.

CONSTRUCTION OF $Na_2HPO_4 12H_2O$ CURVES. (Fig. 130, p. 546.)

The humidities determining curve *AB* are calculated from the decomposition pressures [1] (P) of $Na_2HPO_4 \cdot 12H_2O$ at various temperatures [2] and from the pressures (P_0) of water at the same temperatures [3] as shown by the relationship, $H = \frac{18(P)}{29(760-P)}$. The results are given in Table I.

TABLE I

t	P	$Na_2HPO_4 12H_2O$		H_0	Per Cent Humidity
		H	P_0		
42.2	4.61	0.00378	7.39	0.00610	62.0
51.5	6.38	0.00526	9.69	0.00800	65.7
59.0	8.84	0.00730	12.73	0.01056	69.1
63.1	10.53	0.00872	14.70	0.01228	71.0
68.3	13.09	0.01087	17.56	0.01470	73.9
73.4	16.19	0.01350	21.0	0.01764	76.5
80.6	21.58	0.01814	26.5	0.02243	80.8

For nomenclature, see p. 557.

[1] All values of pressures are given in mm. of mercury.
[2] Frowein, *Z. physik. Chem.*, **1**, 1 (1887).
[3] Scheel and Heuse, *Ann. Physik.* (4), **31**, 715–730 (1910.)

In determining curve *CB* the humidity of air in equilibrium with the saturated solution (H_s) is calculated as before, and expressed in terms of that of air saturated at the same temperature.

The vapor pressures of the saturated solutions at the temperatures of saturation, however, have not been determined, and must be obtained indirectly. The solubilities (J), *i.e.*, the composition of the saturated solution at any temperature [1] and the pressures (P_{760}) of solutions of varying strength at 212° F.[2] are available. Making use of the fact brought out in the discussion of Evaporation (p. 428) that the relative vapor pressure lowering of any solution not too concentrated is independent of the temperature, one can calculate the relative lowering from the data at 212°, and then obtain the pressure at the saturation point (p_s) from the pressure (P_0) of pure water at the saturation temperature. These steps are indicated in Table II.

TABLE II

t	J	$760-P_{760}$	$\frac{100(760-P_{760})}{760}$	P_0	P_0-P_s	P_s	H_s	H_0	Per Cent Humidity
30.4	1.9	3.23	.425	4.29	.02	4.27	0.00351	0.00352	99.6
32	2.5	4.25	.559	4.58	.03	4.55	0.00374	0.00376	99.3
50	3.9	6.62	.871	9.18	.08	9.10	0.00752	0.00758	99.2
68	9.3	15.78	2.076	17.41	.36	17.05	0.01425	0.01454	98.0
86	24.1	38.2	5.03	31.56	1.59	29.97	0.02547	0.02690	94.7

t = ° Fahrenheit.
J = grams anhydrous salt/100 grs. water in saturated solution.
$760-P_{760}$ = vapor pressure lowering at 42° F., mm. of mercury.
$\frac{100(760-P_{760})}{760}$ = per cent vapor pressure lowering.
P_0 = pressure pure water, mm. of mercury
P = pressure of solid duodecahydrate, mm. of mercury.
H_0 = humidity of saturated air, lbs. water vapor per lb. dry air.
H = humidity of air in equilibrium with duodecahydrate.
P_s = pressure of saturated solution, mm. of mercury.
H_s = humidity of air in equilibrium with saturated solution.

[1] Mulder, Bijdragen tot de geschiedenis van het scheikundig gebonden water, Rotterdam (1864).
[2] Tammann, Mem. Acad. Petersburg, **7**, 35 (1887).

CHAPTER XVII

DISTILLATION

INTRODUCTION

In Chapter XII the phenomena of vapor pressure were discussed in detail, and it was pointed out that if two substances at any temperature possessed a marked difference in their vapor pressures, this difference could be made the basis of a method of separation of the two; and if one or both of the substances were recovered by condensation, the process was called *distillation*.[1]

Vapor Composition.—As there explained, an equilibrium is established at any temperature between a liquid or a mixture of liquids held in a containing vessel, and the vapor existing above it. Since it is this vapor which ultimately passes out of the containing vessel and when condensed forms the product of the process, the question arises, what is the relation of the composition of this vapor to the composition of the liquid from which it came and with which it is in equilibrium? The answer to this question is different for different kinds of mixtures; and to comprehend the problems of distillation, these kinds of mixtures must be considered from this point of view.

Liquids with but one Volatile Component.—Obviously, if a volatile component is to be separated from a non-volatile one, the operation is comparatively simple, and has in principle been described under Evaporation on page 380. It is necessary only to volatilize it in one vessel and to condense it in another to accomplish this purpose.

Immiscible Liquids.—In a mechanical mixture of two mutually insoluble liquids sufficiently well agitated to prevent strat-

[1] Destructive distillation may be described as a thermal decomposition of non-volatile material with the formation of products which lend themselves to separation by the methods here described.

ification (for example turpentine and water, heavy fatty acids and water), a dynamic equilibrium is established between the liquid and the vapor when the number of each kind of molecules leaving the liquid is just balanced by the number of molecules of each kind again entering the liquid. Since they are not mutually soluble, each liquid will exert a vapor pressure of its own just as though it alone were present. The pressure existing over the liquid mixture will, therefore, be the sum of these individual pressures, and it follows that a pressure *equal to the atmosphere will be reached and boiling therefore result, at a temperature below that at which either of the component liquids would boil alone.*[1]

The relative amount of the components in the vapor as it passes into the condenser depends upon the relative volatilities of the components as measured by their vapor pressures, and hence is independent of the amount of the components present in the liquid. If in a mixture of liquids A and B (or more), the partial pressures are p_A and p_B and the molecular weights in the vapor form are M_A and M_B, then the ratio of the weights of the components in the vapor is

$$\frac{W_A}{W_B} = \frac{p_A M_A}{p_B M_B}.$$

These facts form the basis of a highly important type of distillation in which a high-boiling liquid is distilled at a comparatively low temperature by the injection of some low-boiling immiscible liquid or its vapor into the still. (See Steam Distillation, p. 565.)

Mutually Soluble Liquids.—Referring again to Chapter XII, it is noted that where two liquids are mutually soluble, the vapor pressure of each is decreased by the presence of the other, and therefore the sum of their vapor pressures is less than the sum of the vapor pressures of the two liquids before mixing. In this case the composition of the vapor is not independent of the relative amount of the components of the mixture, but is profoundly influenced thereby. Sometimes this composition can be

[1] If the liquids be to any extent mutually soluble, the individual vapor pressures are decreased, and the mixture must be heated to a higher temperature to reach its boiling point. See pp. 382 to 385.

calculated from the known vapor pressures of the individual pure liquids. When the molecules of two liquids are of relatively the same size, and when there are no complicated effects when mutually dissolved, such as molecular association, chemical reaction and the like, the composition of the vapor is given by what is known as *Raoult's law*. This law states that that part of the total vapor pressure of a solution of two liquids which is caused by one of the components will equal the product of the vapor pressure of that component in its pure state, and its mol-fraction in the liquid.[1]

This law, together with *Henry's law* will be further discussed and applied in the design of distillation apparatus on page 576 *et seq.* But it may be said that in general the composition of the vapor arising from a solution of one liquid in another is an empirical function of the composition of the solution and must be experimentally determined.

Underlying Principles of Separation.—Certain generalizations may be drawn from the facts just presented that are helpful in obtaining a survey of those processes of separation through distillation where two or more volatile components are involved.

Assume a solution of two liquids, such as benzene and toluene, or alcohol and water, in which one component has a larger vapor pressure than the other. Although the presence of one component will decrease the vapor pressure of the other, yet the vapor arising from the liquid will normally be richer in the lower boiling component than the liquid from which it comes,—roughly in the proportion of their individual vapor pressures. If this relationship between the composition of the liquid, the boiling point of the liquid and the composition of vapor in equilibrium with the liquid at its boiling point be plotted, a possible method of separating the components becomes evident.

[1] By mol-fraction (mol per cent divided by 100) is meant that fraction of the entire number of molecules making up the liquid which is represented by the molecules of the component under consideration. It is obtained from the weight per cent composition z of a liquid by the following equation:

$$\text{Mol-fraction of } A = \frac{\frac{z_A}{M_A}}{\frac{z_A}{M_A} + \frac{z_B}{M_B} + \frac{z_C}{M_C} + \text{etc}}$$

In Fig. 133 is shown as curve ABC the boiling points at atmospheric pressure of all mixtures of benzene and toluene from pure benzene (100 weight per cent of benzene) at the right, to pure toluene (zero per cent benzene) at the left. A second curve ADC, can be constructed from empirical data which will show by following a horizontal line, the composition of the vapor in equilibrium with any mixture of the two components at its boiling point. Suppose, for example, a mixture of 20 per cent benzene and 80 per cent toluene be heated. It will boil when the temperature reaches the point E (101° C.) on the curve, and the vapor which comes off will have the composition represented

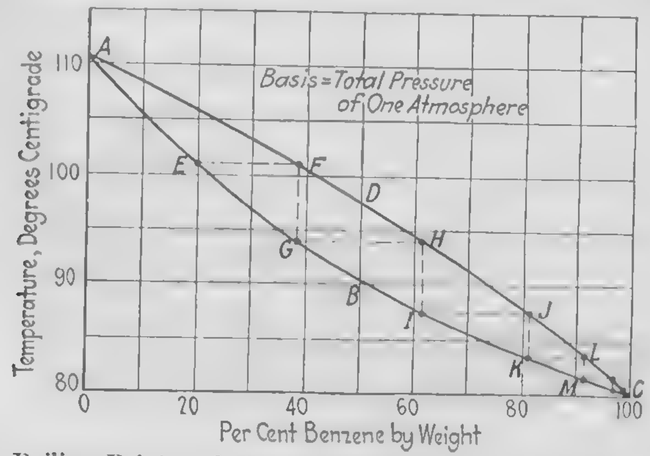


FIG. 133.—Boiling Point and Vapor Composition vs. Liquid Composition. Curves for Mixtures of Benzene and Toluene.

by the point F on the second curve. This vapor if condensed would give a liquid of the composition 38 per cent benzene and 62 per cent toluene. Obviously the liquid remaining in the still will now contain less than 20 per cent benzene and will boil at a higher temperature, that is, further up the curve ABC, and will yield a vapor of a composition determined by the curve ADC. It is seen that while by such an operation the distillate will at any time be richer in the lower boiling component than the liquid remaining in the still, *complete* separation is impossible.

If, now, the vapor which was given off when the liquid boiled at temperature E and which in composition is represented by F, be condensed and heated by itself, it will boil at temperature G and give off vapor having the composition H. If this in turn be condensed and again heated, it will boil at I producing a

vapor of the composition J; and so on until almost pure benzene is obtained near C. Or, what amounts to the same thing, if the vapor formed at E with the composition F be cooled from the temperature at F (101° C.) to the temperature at G (94° C.), vapor of the composition H much richer in benzene will persist, and the remainder of the vapor will condense to form a liquid poorer in benzene with the composition corresponding to G. Thus by controlled condensation the same result will be obtained as by complete condensation followed by revaporization.

When the vapor of composition H falls in temperature to the point I, some of it will condense to a liquid poorer in benzene than that represented by I, by the amount of benzene which has remained in vapor form of the composition represented by J. This liquid poorer in benzene than I will, if returned to the still, immediately boil, again taking heat from the still. When the vapor of composition F falls in temperature to the point G and partly condenses, it must give off heat equal to the heat of condensation of the liquid formed. If now the liquid condensing at I, which is richer in benzene than that condensing at G, can come in contact with the vapors condensing at G, the heat of condensation here set free will immediately boil the liquid condensing at I, and no heat will be taken from the still. In other words, the hot vapor rich in toluene will boil the cooler liquid rich in benzene, forming from the first a liquid yet richer in toluene, and from the latter a vapor yet richer in benzene without the consumption of more heat from the still.

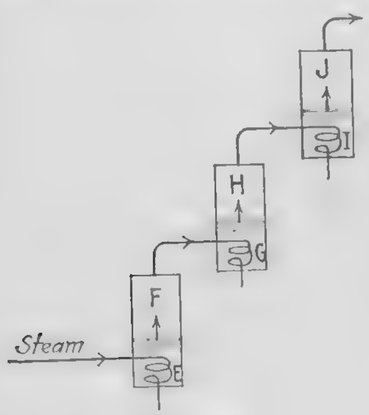


FIG. 134.

An apparatus in which these conditions are realized is shown in Fig. 134, where E, G and I are stills, each supplied with a heating coil and a discharge for the vapor, and in which are placed mixtures of benzene and toluene having the composition represented by the points E, G and I corresponding to the boiling points E, G and I on the curve ABC in Fig. 133, p. 561. The coil in E is heated by steam which boils the liquid of the composition E, evolving vapor of the composition F, at the temperature of E, which passes into the heating coil of the still G. Here the vapor condenses and liquid of the composition F runs out of the coil into a receiver. But the condensing vapor in the coil boils the liquid in G, and vapor of the composition H passes into the coil of the still I, and so on. In this way successive stills will deliver vapor ever richer in benzene until, if enough be employed, almost pure benzene will be obtained.

But the effluent from the coils in the still G is of the same composition as the contents of still G and can be added to it. Since this is the case, one can as well allow the vapor from still E to pass directly into still G and condense therein a liquid richer in toluene and evolve a vapor richer in benzene.

An apparatus in which this direct interchange of heat and consequent condensation and evaporation can take place is called a *rectifying column*, and the process carried on within it is called *rectification*.

Such a system is shown in Fig. 135, where S is a still body or kettle. Resting on the outlet of the still is a column divided into compartments by plates perforated with small holes. Each plate has an overflow pipe discharging into a pool of liquid on the plate below. The layer of liquid on each plate is prevented from passing down through the holes by vapor which is passing up through these holes, from the compartment next below. Any excess liquid accummulating on the plate flows down through the overflow pipe. The letters on the apparatus correspond to those on Fig. 133, p. 561. Vapor from the still at temperature E and composition F passes up and partly condenses at temperature G in compartment G, with a composition slightly poorer in benzene than that corresponding to G. Here is evolved vapor of the composition H which bubbles up through the liquid on the next higher plate which is richer in benzene, with the composition I. Here again condensation takes place at the temperature of I and the heat evolved sends off vapor of composition J, even richer

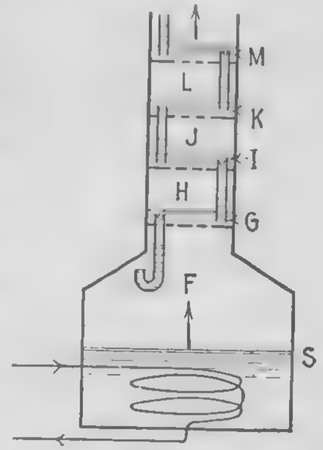


FIG. 135.

in benzene. This can be repeated any number of times, and the vapor finally issuing from the apparatus at the top and into the condenser is practically pure benzene. As in the previous illustration, each one of the compartments in the column may be considered a small still in which the source of heat is the hot vapor coming from below, and the cooling element (condenser) is the cooler liquid from the plate above.

The relationship here pictured is in fact valid only in case the molal ratio of liquid overflowing from plate to plate to the vapor rising through the plates is practically unity, *i.e.*, the ratio of distillate to liquid vaporized is exceedingly small. In practice less overflow must be employed to reduce the heat consumption, and the rate of enrichment is much less rapid than that indicated in the explanation. This special case is discussed here because it brings out clearly the nature of the underlying phenomena. It corresponds to the asymptote of Fig. 160, p. 621.

Liquid Mixtures with Constant Boiling Point.—It sometimes happens that a mixture of two mutually soluble liquids will evolve a vapor richer in the lower boiling one for all compositions up to a definite point. At this definite composition the vapor in equilibrium with the liquid has the *same composition* as the liquid. A mixture of this definite composition will then continue to boil at one temperature without effecting any separation of the two components, even though they possess different vapor pressures when in the pure state. Beyond this definite point of concentration, vapor in equilibrium with the liquid is richer in the *higher* boiling component. Such a liquid is said to have a constant boiling point. This phenomenon is a relatively common one, and can best be understood by a consideration of the direct relationship of composition of vapor to composition of liquid discussed at length on pages 589 to 594.

DISTILLATION PROCESSES

One Volatile Component Present in Relatively Large Amount

Volatile Component Low Boiling.—The method and apparatus used in separating a very volatile component when present in large amount from a non-volatile one, are essentially the same

as those described under Evaporation. A surface condenser must here be used, while the operation may be carried on under any desired pressure. The multiple-effect principle is not employed in distillation, usually because the small scale of operation does not justify the expense of such equipment. In distillation practice the stills are usually "pots," either direct-fired, steam-jacketed, or heated by steam coils within them.

Stills similar in construction to the evaporator bodies described on pages 408 to 415 will, on account of better heat transfer coefficients, give greater capacity. The only arguments against the latter are the larger number of joints, with the correspondingly greater danger of leaks through gaskets, especially where organic liquids are being heated, and the much greater difficulty of cleaning out sticky and adherent residues.

The Volatile Component High Boiling; Steam Distillation.—Volatile organic liquids containing non-volatile impurities in relatively small amounts are frequently met, where the boiling point is so high that incipient decomposition may take place if distilled directly at atmospheric pressure. Even where this would not occur upon the distillation of the pure liquid, the impurities may be sufficiently soluble in it that when they are concentrated, the viscosity of the liquid and its boiling point may become so great that local superheating due to imperfect mixing will cause decomposition. Aniline, glycerine, fatty acids recovered from cottonseed foots, and many other materials, illustrate this point. Advantage is here taken of the fact that in a mixture of liquids not mutually soluble the vapor pressures of the components are directly additive. Water or steam is introduced into the still, and the boiling point of the mixture is thus made lower than that of either of the components when alone. Such liquids are then purified by "steam distillation," not only because this lowers the temperature at which the liquid distills, but also because the injected steam keeps the liquid mass thoroughly agitated. Thus aniline, for example, boils at 180° C. under atmospheric pressure. Under a high vacuum it can be boiled at 100°, but such a vacuum may be hard to maintain. If, however, steam be injected into the still at atmospheric pressure, the aniline is heated to approximately 98° where the combined vapor pressures of aniline and water equal one atmosphere, and boiling proceeds, the mixed vapors distilling together. It is

possible to use any inert gas instead of a condensable vapor for the distillation, although in this case the heat must come either from the cooling of the hot gas, or from some external source. Since the gas is saturated with the vapor of the thing distilled when it leaves the condenser, it must be recirculated through a preheater to avoid this loss of vapor from the system.

Steam distillation is generally carried out in a cylindrical still, sometimes externally heated either by steam jacket or direct fire, and with injection of the steam through coils placed in the bottom of the still with numerous perforations to secure uniform distribution.[1] The still must be connected with a condenser for the liquefaction of the mixed vapors, the components of which are separated by gravity. The use of steam is a matter of convenience and cheapness, as other vapors not appreciably soluble in the material to be distilled may thus be employed.

The method for calculating most of the points involved in the design of stills and auxiliaries for steam distillation, such, for example, as the heat quantities which must be supplied in vaporization and removed in condensation, the volumes of vapors and liquids to be handled, the heating and condensing surfaces necessary, etc., are but the application of principles already described, and will be referred to later in this chapter under Design of Distillation Apparatus.

The ratio of the substance distilled to the steam coming over with it is frequently below that calculated from the saturation pressures (see p. 559), owing to imperfect contact of the steam with the substance. If the steam comes through in large bubbles which rise rapidly and the layer of liquid being distilled is shallow, the time of contact in the still may be too small to secure equilibrium between the steam and vapor, and it leaves the still carrying less than the maximum amount of vapor. The equation on page 559 gives, however, a statement of the theoretically possible performance of a still, and thus furnishes an exact measure of the efficiency of the operation.

Steam Distillation in Vacuum.—While most steam distillations are carried out at atmospheric pressure and at less than 100° C., one must occasionally deal with a material of such low

[1] The relation between the number and size of these distributors and the pressure drop and rate of flow through them may be determined by considering the perforations as orifices. See page 53.

volatility that a higher temperature and less than atmospheric pressure must be used. An important illustration is the purification of oleic and other fatty acids by steam distillation where the highest allowable temperature and the lowest obtainable vacuum are desirable.

The steam consumption of such a distillation is in any case strikingly small, but decreases as the vacuum becomes more perfect. Just because liquids of higher volatility, such as aniline, can be steam distilled at atmospheric pressure, is no reason why they should be so distilled. For the greatest economy in steam distillation, the still should be heated from an external source of energy to the highest allowable temperature, and should be operated under as high a vacuum as the cooling water will permit. The only equipment needed in addition to that usually employed is a wet air pump for the removal of the condensed liquid and any permanent gases originally dissolved, or due to leakage of air. As is obvious from ordinary steam condenser practice in power plants, such a pump is cheap both to install and to operate.

In the separation of glycerine from impurities by steam distillation, the volatility of the glycerine is so low that the distillation must be carried out at the best attainable vacuum, and at a high temperature, approximating 180° C. At this temperature and pressure the solubility of water in glycerine is very small, and the vapor pressure of the glycerine is therefore practically that of the pure substance. However, unless separated by fractional condensation, the glycerine and steam condense together as a single liquid mixture and must be separated by a subsequent distillation. Because of the widely different boiling points, little glycerine is then volatilized, and this process is generally called evaporation.

Use of Superheated Steam.—If the substance to be distilled be maintained at the highest allowable temperature by an external source of heat, and at a pressure sufficiently low to prevent the formation of a water layer, the steam consumption of the process is greatly decreased. In the equation,

$$\frac{W_A}{W_B} = \frac{p_A M_A}{p_B M_B},$$

expressing the composition of the vapor, the value of the pressure of the substance to be distilled is its partial pressure at the tem-

perature in the still. The partial pressure of the steam is found by subtracting from the total pressure in the system that of the material being distilled. The total pressure is determined by the cooling water and condensing apparatus employed.

In this type of distillation it is especially important to prevent any condensation of the mixed vapors arising in the still until they have passed the highest point in the goose neck at the top of the still, and are on their way down toward the condenser. Lagging the top of the still is insufficient, as this merely reduces but does not eliminate the evil. The still should, wherever possible, be externally heated up to and above the top. A steam jacket can be used, but such is expensive to construct, is likely to develop leaks, and the realizable temperature is limited by the strength of the still. Where direct firing is used, it is best to allow the flue gases to flow up and over the top of the still at such a temperature as to avoid appreciable superheating of the vapors and yet to prevent all heat loss from the vapor zone.

One Volatile Component Present in Relatively Small Amount; Steam Distillation

The recovery of benzene and toluene from illuminating gas, gasoline from natural gas, and processes of this type, are frequently accomplished by dissolving the vapors in a suitable solvent, such as a heavy paraffin oil or cresol. There is thus produced a solution so dilute with respect to the benzene that removal of the benzene by simple distillation is impractical on account of the high boiling point. The situation is met by distilling the mixture with steam at a temperature so low that the volatility of the oil is negligible. Condensation of the steam and benzene makes possible the separation of the two by gravity.

As the benzene or other vapor is removed from the oil its concentration decreases, and, according to *Henry's law*, its partial pressure decreases proportionately. This means that the necessary quantity of steam progressively increases during the distillation. Since, however, steam saturated with benzene at a low concentration of benzene in oil is still capable of picking up benzene from a solution of higher benzene content, it is obvious that counter-current flow of steam and benzene is demanded. Such counter-current flow is obtained in rectifying columns of the general type described on pages 574 to 577.

The steam consumed in such a process may be greatly reduced by the use of a vacuum, for reasons entirely analogous to those already described; and although a vacuum is not usually employed in this work its desirability is clear.

A study of the rectifying columns mentioned above shows that the pressure on the lower plates is always higher than that on the upper ones by an amount corresponding to the head of the liquid on the plates. This increase of pressure at the bottom of such a column interferes with the removal of the volatile component by the steam. By allowing a free passage for the vapors up through the column, at the same time providing for effective counterflow of the liquid down through the column, this difficulty is reduced to a minimum. For this reason, the tower fillings described on page 576 can here be used to advantage.

Volatile Solid Component; Sublimation

Certain solid substances possess at temperatures below their melting points vapor pressures so high that distillation without melting is practical. This process is called *sublimation* and is used for the separation of solids when only one component is volatile. Except in the respects noted below it does not differ from the distillation of a material containing a single volatile liquid.

If the material sublimed contains only a slight amount of non-volatile impurities the volatilization can be carried out without difficulty in a direct-fired or steam-jacketed still or retort. The material is in immediate contact with the hot wall of the retort and, as it volatilizes, fresh charge comes into contact with the heating surface. If, on the other hand, there is a large percentage of infusible, non-volatile impurity in the material, the escape of the volatile portion which is in immediate contact with the retort wall leaves behind an insulating layer of impurities which makes it difficult to heat the whole mass without danger of localized overheating. In such a case direct contact of every portion of the charge with the retort wall must be effected by some sort of agitation.

The most serious problem in sublimation is in the condensation of the vapors. If a surface condenser be used, the cooling surface

is quickly coated with a layer of the sublimate which insulates the vapors from the condensing surface and greatly reduces the capacity. In some cases the condenser can be equipped with mechanical scrapers, but such an apparatus must generally be made of steel or cast iron and there is danger of contamination of the product. It is usually best to condense the vapors by diluting them with large quantities of cold gas, most frequently air. Where necessary, inert gases can be used for dilution.

If the vapors be cooled very quickly by admission of gas at a temperature far below the sublimation point, the material condenses as an extremely fine powder. When it is desired to produce large crystals, the temperature and quantity of diluent gas must be so controlled that the vapors are not greatly supersaturated. If these vapors be now passed through a large chamber in which strings or other centers for crystallization are suspended, the supersaturated vapor will condense slowly and large crystals will result.

The disadvantage of condensation by dilution is that the gas leaving the condenser chamber is saturated with the vapors of the material sublimed. While the partial pressure of the material at this low temperature may be small, the quantity lost can be large since the molecular weight may be high and the gas quantities very great. These difficulties are met by cooling and recirculating the gas. If, however, a surface cooler be used it will choke up with crystals deposited from the saturated gas. This can be overcome by using a spray cooler, and filtering out the crystals which separate from the water withdrawn from the chamber, or by evaporation if the material be soluble. In the latter case the spray water may be recirculated through a surface cooler. Where the material sublimed is sensitive to water, other suitable liquids, such as organic solvents can be used for the spray cooling, and recirculated through a surface-type water cooler.

In the sublimation of materials sensitive to heat it is sometimes advisable to admit gas or steam in the retort itself to volatilize the material at a temperature below its normal sublimation point, in a way entirely analogous to that used in steam distillation. It is obvious, however, that this introduces additional difficulties in condensation.

Binary Liquid Mixtures, with Components Volatile and Miscible in All Proportions

Simple Distillation.—On page 560 it was stated that a mixture of two liquids which are mutually soluble evolves a vapor, the composition of which is usually different from that of the liquid. If such a liquid mixture be volatilized, its composition will progressively change, leaving the residual liquid poorer in the more volatile component, and the vapor evolved correspondingly richer. But the vapor will not be free from the less volatile component, and the separation will be incomplete. Such a single vaporization used to partially separate two or more volatile liquids will be called *simple distillation.*

Such distillation processes have heretofore been much used in the refining of crude coal tar, petroleum and materials of this kind. The stills consist of very large boiler plate cylindrical vessels with rounded ends and are direct-fired. In the refining of petroleum it is common practice to build these stills in multiple, setting each succeeding still somewhat lower so that the residuum from still 1 may overflow by gravity to still 2, and so on through the series. A more intense fire is maintained under each succeeding still so that there is a temperature gradient from the first to the last, thus producing a series of products of progressively increasing boiling point. The condenser is generally formed from steel pipes made up with return bends into a rectangular coil, which is set in a box holding running water. If the material distilled is such that there is danger of solids lodging in the condenser tubes, the apparatus shown in Fig. 136 is very advantageous. It is made from cast iron or autogenously welded steel pipe and fittings, ending in removable flanges. These flanges should extend beyond the end of the box containing the cooling water, and thus insure easy access for cleaning. When the condensate is insoluble in water and can be easily separated from it by stratification, an efficient and economical condenser is made by passing the vapor and water countercurrent over packing material in a small tower.

The separation of the components in such a still must of necessity be incomplete, and the product is re-run to obtain the fractions sought. More recently such stills are being equipped

with rectifying columns which function as described on page 563, and thus a better separation with larger capacity and less expense of fuel is effected.

The transfer of heat is low in such a still, and in the more modern installations the charge is heated by forcing it at high velocity through a bank of tubes set in a direct-fired high temperature furnace, and discharging the same into a still body where distillation takes place.

Vapor Enrichment; Redistillation.—Since the separation of two volatile liquids by simple distillation is so incomplete, means for its improvement must be developed. In the last analysis there are but two methods of accomplishing this; one is by con-

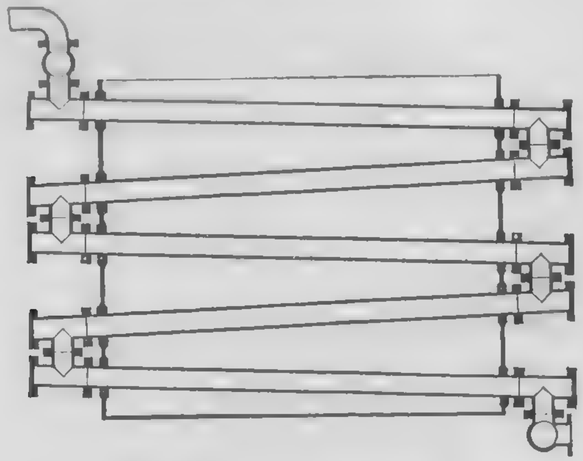


FIG. 136.—Tar Condenser.

densing the vapor obtained from a simple distillation, and revaporizing it, namely, redistillation. The first distillate is richer in volatile component than the original liquid. If this be condensed and redistilled, the second distillate will be yet richer. By repeated redistillation the separation can be carried, theoretically at least, to any desired point. It is obvious, however, that such repeated redistillation involves a large number of steps and a large heat consumption.

Partial Condensation.—The second method for improving the separation is to somewhat cool the mixed vapors from a simple distillation producing a *partial condensation* of the vapor. The liquid condensate formed will be in equilibrium with the remaining vapor from which it separated. From the structure of the

liquid-vapor equilibrium curves on page 590, it will be seen that the condensate will be poorer in volatile component than the remaining vapor, and that the vapor has therefore been enriched in volatile component. In other words, the partial condensation of a vapor has the same sort of effect on its composition as has redistillation. Thus, simple distillation coupled with properly controlled partial condensation is capable of effecting the separation of two volatile liquids as completely (though not as easily or efficiently) as can be done by more complicated distillation processes.

Partial condensers have been built in many forms, one of the older and more simple types consisting of a series of metal bulbs immersed in cooling water, from each of which the condensate collecting therein may be drawn. An ordinary tubular surface condenser may be employed and to insure effective countercurrent action, it should be long relative to its diameter. As explained on page 581, when efficient separation in the condenser itself is desired, it is best not to use it as a preheater, as is often done. Condensers of this type have been built as a combination of plate tower and feed-liquor preheater, but the best results are realized by building tower and condenser separately, each designed to perform its own function. The cooling medium must be under accurate control with a very low temperature difference between it and the condensed vapor, and so far as possible, localized total condensation avoided. For effective partial condensation a large area of condensing surface is required.

Rectification.—A study of the liquid-vapor equilibrium curves shows that the condensate formed upon partial condensation of a vapor is necessarily richer in volatile component than the liquid from which the vapor was originally evolved. Therefore, this condensate cannot be in equilibrium with the vapor rising from the still, and if brought in contact with it some sort of interaction must take place. From the liquid-vapor diagram it is seen that this interaction must involve the condensation from the vapor rising from the still of part of the *less* volatile component with evolution of a new vapor richer in the *more* volatile component. The heat of condensation thus set free tends to raise the temperature of the liquid, but since it is already at its boiling point there results a new vapor in equilibrium with the liquid from which it rises. This interaction of a vapor rising

from the still with the condensate from a part of the vapor previously evolved, is called *rectification.* The combination of partial condensation and rectification with simple distillation affords an efficient means for separating volatile liquids.

Since rectification in its result is equivalent to a series of redistillations without the consumption of additional heat, it is analogous in this respect to multiple effect evaporation; however, it is only the result that is similar and not the mechanism of attaining it.

Definition of Terms.—In the literature of distillation the three terms *dephlegmation, fractionation* and *rectification* are loosely used to describe the different processes or combinations of processes. Usually dephlegmation covers what is above called partial condensation; *i.e.,* the cooling of a mixed vapor to a definite temperature with the resulting condensation of a fraction which contains mainly the high boiling components or *phlegm.* The same term is sometimes applied to what has just been defined as rectification; *i.e.,* to the partial removal of the less volatile component from the vapor by allowing that vapor to interact with the partial condensate from a previous fraction of vapor from the same still. Sometimes dephlegmation refers to the combination of the two processes. Fractionation is generally applied to the combination of these processes and is occasionally used interchangeably with dephlegmation. The term rectification was formerly restricted to the enrichment of the vapors of alcohol-water mixtures to form a strong alcoholic distillate with the concurrent removal of the fusel oil.

As already indicated, the enrichment of a vapor in the more volatile constituent by cooling it sufficiently to separate out as liquid a part of the less volatile component will be here designated *partial condensation;* the interaction of such a partial condensate with the vapor rising through a column from the still, resulting in further enrichment of the vapor in low boiling constituent, will be called *rectification.*

Plate Columns.—In order to be efficient the contact between the vapor rising from the still and the liquid reflux resulting from a previous partial condensation must be counter-current and as intimate as possible. Experience has developed the bubbling plate column as one of the best methods for securing this result. This rectifying column, as it is called, consists of a series of plates

over which flows the liquid reflux and through which the rising vapors are made to bubble. The reflux flows from plate to plate through suitable overflow pipes and the vapor rises through each of the plates in series counter-current to the flow of the liquid.

Such a column is shown in Fig. 137, one plate being shown without the bubbler caps which deflect the vapor underneath the liquid, another plate showing the bubbler caps in section, and a third plate in which may be seen the small openings through which the vapor escapes into the liquid. The height of the overflow pipes regulates the depth of the liquid remaining on each plate, while the lower end is sealed in liquid, thus preventing the vapors from short-circuiting through them.

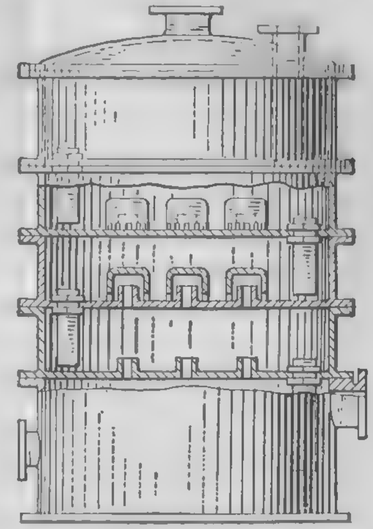


Fig. 137.—Plate Column with Multiple Slotted Caps.

The bubbler caps are of various design, one common type being shown in Fig. 138. This single large cap upon each plate is from some points of view undesirable inasmuch as the vapor escapes only at the periphery of the cap, the entire center being inoperative. Furthermore with such a single bell there is a tendency for the vapor to come out one side and the liquid to flow around the other. A large number of small, circular caps, or better still, long rectangular ones are more efficient. The edges of the cap are often serrated or notched to give smaller bubbles and therefore better contact at low vapor velocity and yet provide a very large cross-section for the escape of the vapor when the column is forced. Obviously the liquid should flow across the

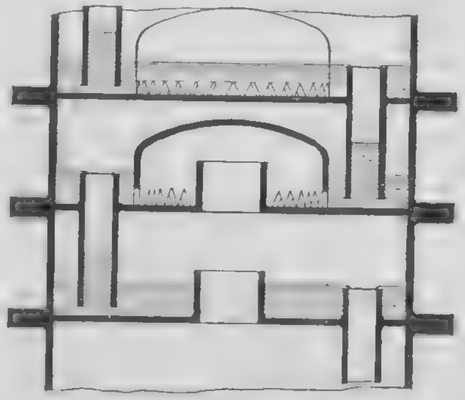


Fig. 138.—Plate Column with Single Caps.

entire diameter of the plate in order to expose it evenly to the rising vapor.

A simple type of plate sometimes employed consists of perforated sheet metal or even of a wire screen, Fig. 135, p. 563. This type has the disadvantage that when the vapor velocity is low the liquid surges through the vapor holes from the plates into the still. Consequently, such a column cannot be operated at low capacity. With a high vapor velocity the friction through the holes is very large and if such a plate be not absolutely level, all the liquid will run through the low side and the vapor pass up the high side. However, these plates when properly placed give a high plate efficiency because of the exceptionally small bubbles produced and their excellent distribution.

The column may be constructed of a single cylindrical shell into which the plates are inserted, or of a series of short flanged sections, each containing one or more plates, bolted together with gaskets. The first type is more difficult to build, and more likely to develop leaks around the plates within the column; the second type is liable to leak through the gaskets between the sections, but possesses the advantage of flexibility in that the height of the column can be varied by the removal or addition of sections. A relatively large pressure is required to force the vapor through the column against the resistance of the orifices and the liquid head, which is a disadvantage in many gas washing operations; but this disadvantage disappears in distillation because the necessary pressure can be easily developed within the still by merely allowing the temperature of the boiling liquid to rise. (But see p. 578.)

Tower Fillings.—The interaction between vapor and refluxing condensate can be efficiently secured by the use of a plain tower filled with suitable packing material over the surface of which the reflux flows to the still and through the voids of which the vapor rises. When dealing with excessively corrosive liquids, as for example in the separation of nitric and sulphuric acids,[1] such

[1] Nitric acid may be efficiently concentrated by mixing it with strong sulphuric acid, and allowing this mixture to flow down a filled tower against an ascending current of steam. The heat of condensation of the steam combined with the heat of dilution of the sulphuric acid distills the nitric acid. The fractionating effect of the tower enables the operator to withdraw concentrated acid from the top of the tower and completely denitrated sulphuric acid from the bottom.

a tower can be built of resistant material and filled with broken quartz. A number of tower fillings made from refractory earthenware have been developed, all designed to present a large surface of contact between vapor and liquid to avoid the formation of channels through which the liquor may pass undisturbed by the vapor, and to develop as little back pressure as possible. Of these it seems probable that the best are short hollow cylinders of a length equal to diameter. Peters[1] has shown that if these cylinders are made quite small (even as small as one inch) their efficiency increases so rapidly with decrease in size that the column may be made shorter and thus compensate for the increased resistance to the vapor per unit length. One must here strike a balance between the large area exposed by small units and the high resistance to the moving vapor occasioned by them. The greater velocity of the moving vapor favors complete interaction between vapor and liquid because of the constant destruction of the stationary film which tends to form. (See Fluid Films, p. 36.)

A very popular device of this type is a cylinder of earthenware having a diameter equal to its height and containing a short helical core. These rings are thrown into the tower at random, their uniform size and dimensions insuring an even, homogeneous packing. The area presented for reaction is large, while the frictional resistance to the moving vapor is small.

Distribution of Reflux.—An even and uniform distribution of the partial condensate over the top of the tower filling is controlling in the efficient operation of such a tower, especially if it be relatively short. There exists a strong tendency for the ascending vapor to seek out channels of least resistance, and these "chimneys" once formed seem to perpetuate themselves, allowing the liquid to flow down undisturbed. Davis[2] illustrates a distributor which for some purposes possesses great merit, in that, by means of a siphon, a "slug" of liquid is delivered at stated short intervals. The liquid at first entirely floods the filling but is immediately broken up by the vapor and descends uniformly distributed over the entire cross-section.

Rectification under Vacuum.—If the operating temperature in a rectifying tower must not exceed a low maximum, as in the

[1] W. A. Peters, Jr., *J. Ind. Eng. Chem.*, **14**, 6, 476 (June, 1922).

[2] "Handbook of Chemical Engineering," vol. 2, 220 (1904).

dealcoholizing of beer, a vacuum must be maintained in the system. Under this condition a tower or column with an open filling to give the least frictional resistance to the flow of vapor is better than a column equipped with plates. (See p. 569.)

Condensers.—A rectifying column can be operated only in connection with the still below and a condenser above it, and the behavior of each of these influences its own performance. It has already been pointed out that with a partial condenser, properly designed and operated, a column though desirable, is unnecessary. In general, the better the partial condenser the less work there is for the column to do, and the work of separation can within certain limits be divided between the two units at will. If a rectifying column be found inadequate for the task in hand, separation may be made more complete by increasing the amount of reflux from the partial condenser. This may be effected by either increasing the volume of cooling water or dropping its temperature. However, as previously stated, this increases the heat consumption of the still.

This interchangeability of function of the partial condenser and the rectifying column makes it possible to compensate for an inefficient partial condenser by using a somewhat taller column. Furthermore, since a highly efficient type of partial condenser is expensive to construct, sensitive to fluctuating conditions, and difficult to operate, it is in many cases advisable to make no attempt to effect separation in the partial condenser itself, but to use it simply to produce the proper reflux for the column and to compensate for this inefficiency by the use of a few more plates. (See Fig. 160, p. 621.) This makes it possible to use the partial condenser as a heat exchanger for preheating the liquid feed.

To attain simplicity in operation it is possible to omit the partial condenser altogether and employ a final condenser which completely liquefies all vapor leaving the column, a part of this condensate being deflected as reflux to the column and the rest taken off as product. It is, however, difficult to construct and operate a single condenser of this type which will both cool the product and at the same time preheat the feed. It is usually better practice to employ a single condenser for the production of reflux and product, cooling the latter in a liquor cooler.

Where the vapor is insoluble in water the final condenser

may be of the jet condenser type. If the heat to be absorbed is large and the condensate separates readily from water, as in the refining of heavy petroleum oil, a small tower packed with Raschig or similar earthenware rings, over which cooling water flows, is both inexpensive and efficient in its condensing action.

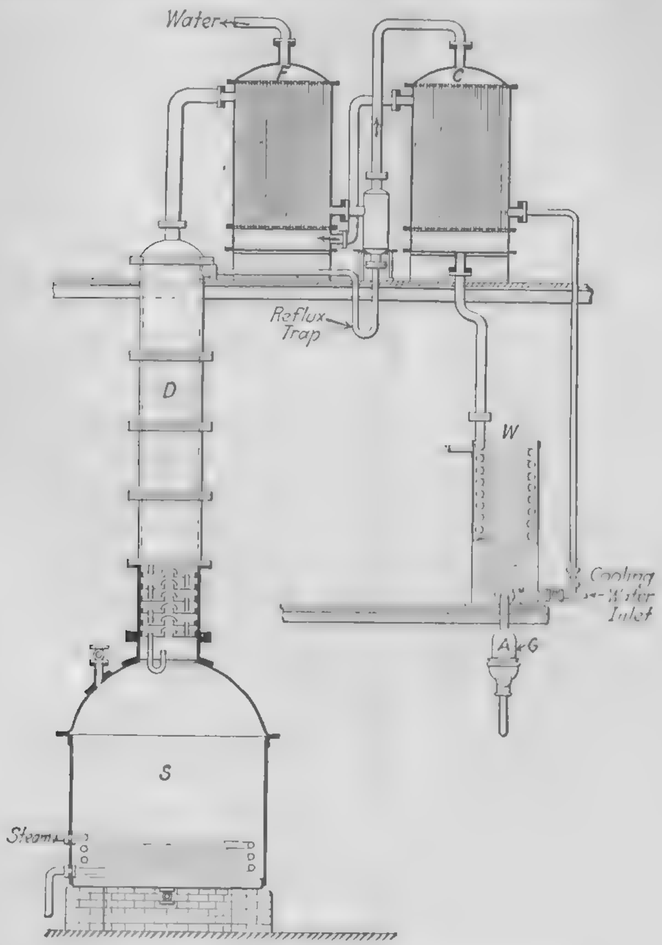


FIG. 139.—Intermittent Column and Still.

Intermittent Operation of Distillation Apparatus.—A rectifying apparatus can be operated in two fundamentally different ways. In *intermittent operation* the still below the column is filled with a charge of the liquids to be separated (*e.g.*, benzene and toluene), and distillation begun. In Fig. 139, *S* is the still, *D* the rectifying column, *F* the partial condenser, *C* the final condenser, and *W* an auxiliary cooler for the product. *G* is a glass dome covering

the overflow chamber A, where the rate of distillation can be observed, and where a hydrometer may float, indicating at all times the gravity of the liquid product. As a volatile constituent (benzene) is removed, the residuum in the still becomes progressively richer in the less volatile substance (toluene). This means that the vapor rising from the still grows continually poorer in benzene, and hence to free it from toluene, since the rectifying column is of a fixed length, the ratio of condensate refluxed at the top of the column to the distillate must be progressively increased. This is accomplished by controlling the temperature and amount of cooling water in the partial condenser. This necessity for continually modifying the operating conditions in an intermittent distillation is a serious disadvantage, but satisfactory separation of the constituents can be realized, except at the very end of the operation, when the distillate always contains some of the higher boiling constituent, and must be collected separately for admixture with the next charge. This inability to effect complete separation at the end of the operation is occasioned by the fact that there is insufficient low boiling component in the system to maintain the necessary concentration gradient through the column; *i.e.*, there remains only the high boiling component on the bottom plates. The effective length of the column is thus reduced below that essential for complete separation. (See p. 600.)

Continuous Operation of Distillation Apparatus.—Just before the end of the operation in an intermittent unit as above considered, toluene exists in the still free from benzene, while there is being discharged from the condenser practically pure benzene. The percentage of benzene in the vapor and liquid in the column increases progressively from the bottom to the top plate. Assume that the original feed to be separated contains 80 per cent of benzene. On some plate near the middle of the column a liquid of practically this composition will be found. If now the feed containing 80 per cent of benzene be introduced continuously onto this plate, the conditions in the system will tend to perpetuate themselves; *i.e.*, concentrations at all points will remain unchanged, benzene will be discharged from the final condenser while toluene will work its way down into the still from which it may be continuously withdrawn. This method of distillation is called *continuous rectification*. It may be shown mathematically that the heat efficiency of a continuous operation is greater than that of an intermittent operation, while as above noted, the operating conditions are less complicated. Intermittent rectification is justified only when working on such a small scale, or under such other conditions as to make continuity of operation impossible.

Heat Recovery.—Rectification, especially if continuous, offers various opportunities for the economy of heat through the use of heat economizers or exchangers. The best "routing" of the feed through the heat-recovery system varies with conditions, but where a short column in conjunction with an efficient partial condenser is employed, the arrangement shown in Fig. 140 is useful.

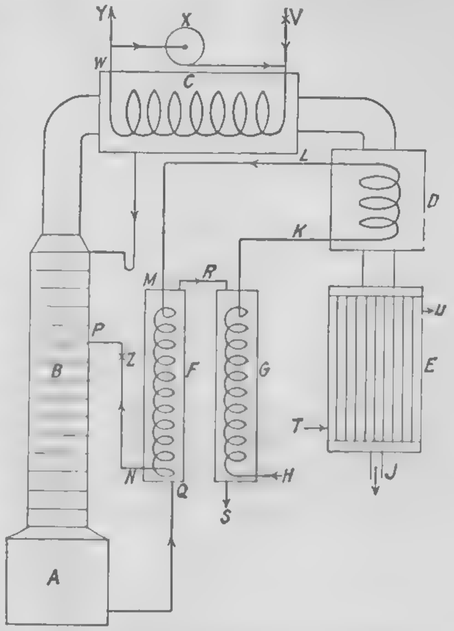


FIG. 140.—Heat Recovery System for Continuous Distillation.

In this arrangement the cold feed liquor enters the system through the coil G at H, where it is warmed by the somewhat cooled discharge from the still A as it flows from the heat exchanger F. The feed then acts as the cooling medium for the preliminary condenser D, leaving at L and entering the final preheater or heat exchanger F, through which flows the less volatile constituent of the charge at its boiling temperature as it leaves the still. When the difference in the volatilities of the components of the charge is large, it sometimes happens that the feed leaves the heat exchanger F at N actually superheated. This necessitates a throttle valve Z located just before the feed enters the column at P. The volatile component is completely condensed in E fed with cold water at T. The use of feed in the partial condenser C is generally inadvisable, because the unavoidable variation in its amount and temperature render impossible that delicacy in control of the amount and temperature of the cooling medium so essential in efficient partial condensation.

In such a case, it is better to recirculate at a high velocity the cooling water[1] in the partial condenser by means of the pump X, controlling the temperature by admitting cold water through the valve V, allowing a corresponding amount of hot water to waste at Y. This requires a large condensing surface but may be justified by the increased efficiency of the entire apparatus.

DESIGN OF DISTILLATION APPARATUS

The quantitative relationships of the vapor pressures of liquid mixtures are extremely complex except under conditions of constant temperature, and unfortunately these conditions are not those met in practice. Furthermore, wide deviations from the mathematical expressions of these relationships are very common, requiring, in most cases, a solution based upon empirical *laboratory* data. (See p. 591.)

On the other hand, certain quantitative relationships may be established which are valid in some important cases, and which apply within narrow limits to a great many cases. And, possibly more important, the laws which may thus be laid down serve as valuable criteria for estimating the normal behavior of a distillation process, and help to clarify and explain the divergencies which are frequently noted. Therefore in the following discussion isothermal conditions are considered first, after which is given an analysis of constant pressure operations of a character sufficiently general to serve as the basis of the solution of most industrial problems in distillation.

Vapor Pressures of Completely Miscible Binary Liquid Mixtures at Constant Temperature

Raoult's Law.—When one liquid is dissolved in another, the partial pressure of each is decreased. Assume two liquids, the molecules of which are the same size, which mix without the complicating effects of molecular association, chemical combination and the like. In an equimolecular mixture of two such liquids, each unit of surface area of the liquid mixture will have in its face

[1] Where the partial condenser must be operated at a high temperature, kerosene or other high boiling liquid may be used instead of water.

half as many molecules of each component as exist in the liquid surface of that component in the pure state. Hence, the escaping tendency or vapor pressure of each component in the mixture will be half that of the same component in the pure state. Similarly, in a mixture containing 25 mol-percent of the first component and 75 mol-percent of the second, the first will exert a partial pressure 25 per cent of that of this component in the pure state. Therefore, in more general terms for any such mixture, the partial pressure of any component will equal the vapor pressure of that component in the pure state times its mol-fraction in the liquid mixture. This generalization is known

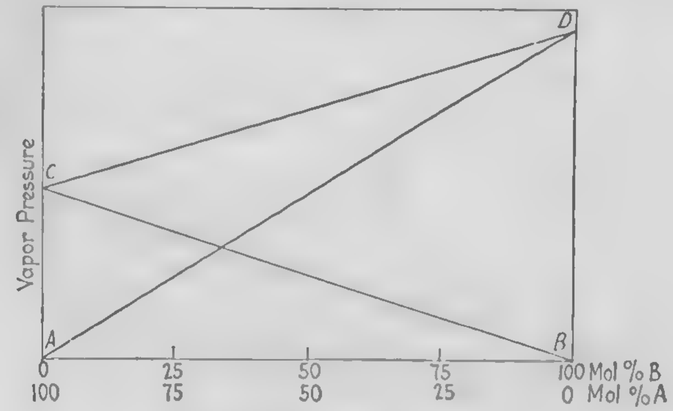


Fig. 141.—Raoult's Law.

as *Raoult's law*. It is expressed in the relationship, $p = Px$, where p is the partial pressure of the component A in the solution, x is its mol-fraction in the solution, and P is the vapor pressure of the component A in its pure state. If P' be the vapor pressure of pure B, and p' that in the mixture, $p' = P'(1-x)$. This relationship is shown graphically in Fig. 141, where the abscissas are the mol-percent or mol-fraction of the two components, A and B, in the liquid portion. The ordinates are pressures, C being the vapor pressure of pure A, and D that of pure B. The lines AD and BC represent the partial pressures of the components over any mixture, while the line CD is a total pressure of the mixture.

Deviations from Raoult's Law.—In view of the above assumptions as to equal molecular size, absence of association, etc., it is not surprising to find Raoult's law honored more in the breach than in the observance. None the less some organic liquids, such

as benzene-toluene, deviate from it but little. The deviations of mixtures of hydrocarbons of the same series can usually be neglected for a great deal of engineering work, and even for mixtures of a number of series this is often true. For mixtures of aromatic and aliphatic compounds, however, the deviations are often large, though never of the order of magnitude of such mixtures as hydrochloric acid and water, and the like. Organic stereoisomers obey it quantitatively as would be expected from the considerations upon which it is based. However, the great majority of other liquids when plotted as shown in Fig. 141 deviate largely from the lines BC and AD except when very near to the points C and D; *i.e.*, the deviation for any component is slight (except where dissociation is involved) if that component be present in very large amount. This is ordinarily expressed by saying that in dilute solutions Raoult's law applies to the *solvent*. Since the deviation from Raoult's law may be either positive or negative, great or small, where results are presented graphically this generalization serves as a convenient standard of comparison.

Henry's Law.—A modification of Raoult's law applies to the vapor pressure of the *solute* in dilute solutions, just as Raoult's law applies to that of the *solvent*. Henry's law states that the partial pressure of the solute is proportional to its concentration in the solution. In analogy with Raoult's law it may be expressed by the equation, $p=kx$, where p is a partial pressure of the solute, x is its mol-fraction, and k is an experimentally determined constant. Comparison with Raoult's law ($p=Px$) shows that they differ only in the constant which determines the slope of the line. This constant is P in the one case, while it must be experimentally determined in the other. A typical vapor pressure curve for one component of a liquid mixture is shown in Fig. 142, where AD is the range over which Henry's law applies, while Raoult's law holds over the section EC, where C is the vapor pressure of pure B.

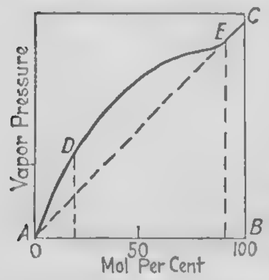


FIG. 142.—Henry's Law.

Volatility.—The term "volatility" is loosely used in the literature, generally as equivalent to vapor pressure when applied to a pure substance; as applied to mixtures its significance is very indefinite. Because of the convenience of the term the volatility of any substance in a homogeneous liquid will be defined as its partial pressure in the vapor in equilibrium with that liquid, divided by its mol-fraction in the liquid. If the substance be in the pure state its mol-fraction is unity and its volatility is identical with its vapor pressure. If the substance exists in a liquid mixture which follows Raoult's law its volatility as thus defined is still obviously equal to its vapor pressure in the pure state, *i.e.*, its volatility is *normal*. If the partial pressure of the substance be lower than that corresponding to Raoult's law, as for example, that of hydrochloric acid in dilute aqueous solutions, the volatility according to this definition is less than that of the pure substance, *i.e.*, is abnormally low. Similarly, if the partial pressure be greater than that indicated by Raoult's law, *e.g.*, that of aniline dissolved in water, the volatility is abnormally high. The volatility of a substance in mixtures is therefore not necessarily constant even at constant temperature but depends on the character and amount of the components.

Relative volatility is the volatility of one component divided by that of another. Since the volatility of the first component of a mixture, v_1, is its partial pressure, p_1, divided by its mol-fraction, x, and that of the second, $v_2=p_2/(1-x)$, the volatility of the first relative to the second is $v_1/v_2=p_1(1-x)/p_2x$. Since the relative amount in the vapor of the components of any mixture (expressed in mols) is $y/(1-y)=p_1/p_2$,

$$\frac{v_1}{v_2}=\left(\frac{y}{1-y}\right)\left(\frac{1-x}{x}\right)=\alpha.$$

In any constant boiling homogeneous liquid mixture the composition of the liquid is identical with that of the vapor in equilibrium with it, *i.e.*, $x=y$; hence the relative volatilities are identical.

Volatility, like vapor pressure, increases rapidly with rise in temperature. The *ratio* of the pressures of pure substances does not change rapidly with change in temperature and the same is true of relative volatilities, but, whereas vapor pressures always increase with temperature, *relative volatility* may, in a given case, either rise or fall, depending on the nature of the components. Relative volatility is the most important factor in determining case of separation of components by distillation.

Duhem-Margules Equation.—A general isothermal relationship based upon the second law of thermodynamics and upon the gas laws, and hence approximately applicable to all mixtures, is the Duhem-Margules equation,

$$dlnp_1/dlnp_2=-(1-x)/x.$$

It can be used as a check upon the accuracy of empirical determinations of vapor compositions, but is otherwise of little practical help. Assume a solution where Raoult's law applies to the solvent. Differentiating the equation of Raoult's law, $p_2=P_2(1-x)$, and substituting in the Duhem-Margules equation, one obtains upon integration $p_1=kx$. In other words, if one component of a mixture obeys Raoult's law over a definite range, within that range the other component must follow Henry's law.

[1] G. N. LEWIS, *J. Am. Chem. Soc.*, **28**, 569 (1906).

Partly Miscible Liquids at Constant Temperature

In those ranges of concentration within which incompletely miscible liquids are soluble in each other, they fall under the preceding classification. As soon as the limits of solubility are exceeded, the two liquids exist as separate layers or phases side by side, each being a saturated solution of the other in itself. The vapor pressure of each phase is exerted independently of the presence of the other, and since the two phases are in equilibrium, the partial pressure of either component in one phase must equal that of the same component in the other. These facts are represented graphically in Fig. 143. The limit of solubility of B in A

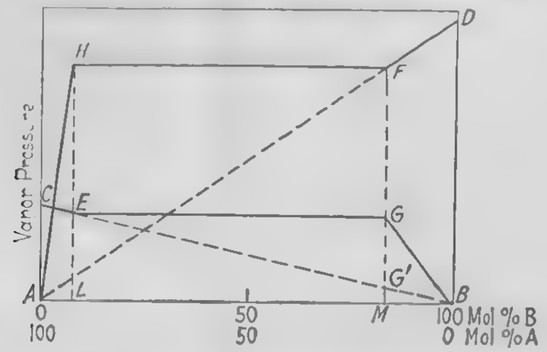


Fig. 143.—Diagram for Partly Miscible Liquids at Constant Temperature.

corresponds to the point L, while the solubility of A and B is given by the point M. Between L and M the components exist as two layers of liquids. The vapor pressure curve of A starting from C may be assumed to follow Raoult's law (the full line) down to the saturation point E, provided the solubility be small. From here to G, *i.e.*, throughout the range in which the two liquids are present as separate phases, and where the compositions of these liquid phases are therefore constant, the partial pressure remains constant, and is represented by the horizontal straight line, EG; from G to B the relationship may be assumed linear (Henry's law). Analogous relationships exist for component B.

The two points of importance regarding this diagram are, first, constancy of the partial pressures so long as two liquid phases are present, and second, the character and extent of the deviation of Henry's law from Raoult's law in the solutions.

The diagram shows that the vapor pressure of A when dissolved in B is abnormally high, *i.e.*, is much greater than is called for by Raoult's law, the line $G'B$. Immiscibility of two liquids implies that the molecules of one find it difficult to force their way into the other. Thus it requires a relatively high pressure of A to force a relatively small amount of it into B. This is equivalent to saying that when A is dissolved in B, the volatility of A is abnormally high. The diagram shows further that the less the mutual solubility, the more abnormal is the vapor pressure, and hence the greater the volatility of the dissolved component. The practical results of these relationships are shown in the following examples.

Despite the fact that aniline boils 80° C. higher than water, the volatility of aniline in an aqueous solution is greater than that of water, *i.e.*, the vapor given off by such a solution is richer in aniline than the solution itself. If, therefore, one distills an aniline-water solution in a column still, the water is discharged from the bottom substantially free of aniline which is found in the distillate. The vapor from the top of the column is condensed and allowed to run into a separator from which the aniline layer (saturated with water) is withdrawn as product while the water layer (saturated with aniline) returns to the column as reflux.

Another important application is found in the dehydration of organic solvents. Thus while water boils 20° C. higher than benzene, benzene saturated with water can be successfully dehydrated by the distillation of less than 5 per cent of the mixture, as the volatility of the water in the solution is abnormally high.

Assume a binary mixture in which one component when present in small amount exerts an abnormally high pressure. *i.e.*, $p_1 > P_1 x$. Since the value of p_1 when x equals unity must be P_1, the curve becomes abnormally flat, and $dp_1 \leqq P_1 dx$. Combined with the Duhem-Margules equation (p. 579) these inequalities give $-dp_2/p_2 < dx/(1-x)$. In words this means that the fractional lowering of the pressure of the second component must within these limits of concentration be less than that corresponding to Raoult's law, and from this it follows that the curve for the second component must be in general shape the reverse of that for the first component.

If in such a mixture the first component when present in small amount exert a very high partial pressure, conditions may exist in which through certain ranges of dilute solutions its pressure may exceed its pressure in

more concentrated ones. If complete miscibility be assumed, there must result a partial pressure curve such as *AKEFLD* of Fig. 144. From the Duhem-Margules equation, it appears that if $dp_1 = 0$, then $dp_2 = 0$. Hence the second component must be represented by such a curve as *BNHGMC*. If, however, there be produced such solutions as are represented by *E* and *F*, since a component will always pass from a point of high to a point of low partial pressure, the first component will spontaneously distill out of *E* into *F*, and the second component will distill in the opposite direction. This action would concentrate *E* back to *K* and *F* to *L*. In other words, the system will spontaneously separate into two layers having the composition represented by *K* and *L*. The quantity dp_1/dx cannot become less than zero without separation of the components; further, when the volatilities of the components are greater than corresponds to Raoult's law, a tendency to separate is indicated. This tendency changes with the temperature, and a mixture of liquids miscible at one temperature may separate at another.

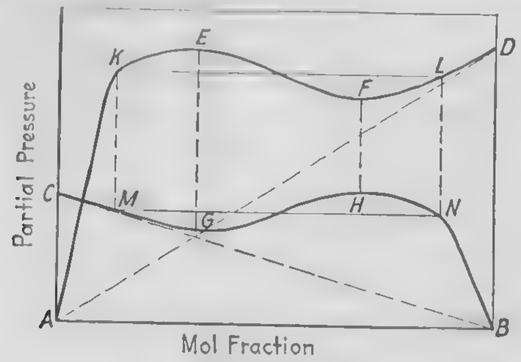


FIG. 144.

Complete immiscibility is the preceding case in which the mutual solubilities are negligibly small and the points *L* and *M* coincide with the points *D* and *C*. The lines *EG* and *HF* would then correspond to the pressures of the pure components *A* and *B*. It is perhaps true that absolute immiscibility never occurs.

If the component present in small amount has an abnormally low partial pressure, $p_1 < P_1 x$, a concentration must be reached at and beyond which $dp_1 \geqq P_1 dx$. Combining this expression with the Duhem-Margules equation, $-dp_2/p_2 > dx/(1-x)$, which states that the fractional increase in p_2 must within this range be abnormally high. Since analogous reasoning applies to the second component it follows that this situation can exist only when p_2 is abnormally low. In other words, in the range in question, if the pressure of one component is very low, that of the other tends to be low and consequently also that of the mixture; there is then a tendency to form a mixture with maximum boiling point.

BINARY LIQUID MIXTURES AT CONSTANT PRESSURE

Boiling Point—Composition Curves.—It follows from the preceding discussion that, if isothermal conditions are to be preserved, arbitrarily predetermined pressure differences must be maintained. This is so impracticable that distillations are never carried out at constant temperature, but rather at constant pressure, and variable temperature. The vapor pressure and boiling point which correspond to any definite liquid mixture are usually plotted as described on p. 561, the abscissas being liquid compositions, and the ordinates boiling points. The abscissas are frequently made mol-percent, undoubtedly through analogy with the Raoult's law diagram; but this complication, which at constant temperature justifies itself by developing certain simple relationships, lacks this advantage in the constant pressure plot. In these boiling-point composition curves, therefore, the abscissas have been plotted as weight per cent.

Liquid-Vapor-Composition Curves.—For the solution of problems the constant-temperature diagram just considered, though frequently used, is inconvenient because it is indirect, and because a change in pressure makes a relatively large error on the vertical temperature scale. The value of greatest interest is the relation between *liquid composition* and *vapor composition*, plotted as shown on curve *A* on the alcohol-water diagram, Fig. 145. This method is advantageous first, because the data are actually obtained in this form as the result of experimentation, and second, because the values thus expressed change but slightly with variation in pressure or temperature. A single curve obtained at an average pressure can generally be used over a pressure range of 20 or 30 per cent with an error of not more than 2 per cent.

Again, assume a mixture of two liquids *A* and *B*, which follow Raoult's law, and in which p_1 is the partial pressure of *A* in a mixture in which the mol-fraction of *A* is x, and p_2 that of *B*. The vapor pressures of pure *A* and *B* are P_1 and P_2 respectively, from which it follows that p_1 equals $P_1 x$ and p_2 equals $P_2(1-x)$. The mol-fraction of component *A* in the *vapor* evolved from this mixture is y. Hence

$$\frac{y}{1-y} = \frac{p_1}{p_2} = \frac{P_1 x}{P_2(1-x)}.$$

This states that the mol-ratio in the vapor is P_1/P_2 times that in the liquid. The ratio P_1/P_2 changes but very little with the temperature, from which it follows that changes in temperature

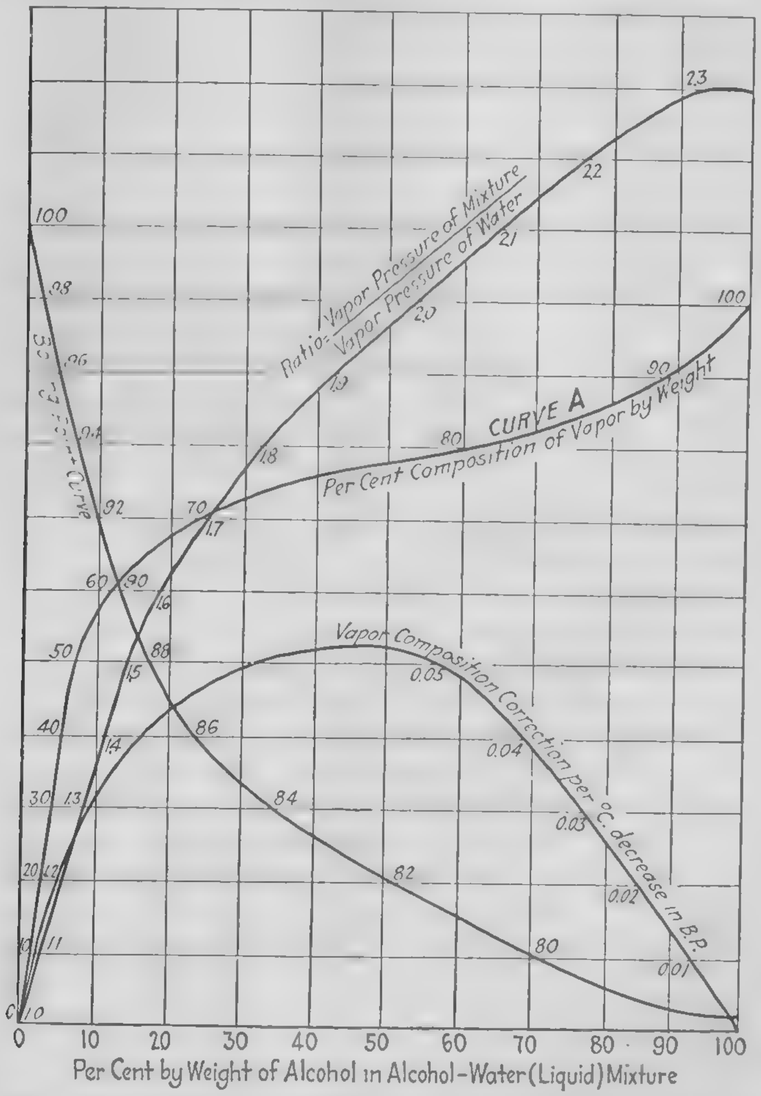


FIG. 145.—Characteristics of Alcohol-water Mixtures. The ratio curve applies to mixtures when at 79.3° C. For any other boiling temperature, t degrees Centigrade, there must be added to the values shown the correction term, 0.000034 times the weight per cent of alcohol in the liquid times $(79.3-t.)$.

have little effect upon vapor composition. Calling the relative volatility $P_1/P_2=\alpha$, the amount of low-boiling constituent is

$$\frac{y}{1-y}=\frac{\alpha x}{1-x}, \quad \text{or} \quad y=\frac{\alpha x}{1+(\alpha-1)x}.$$

It can be shown algebraically that the equation is identical in form, when x represents fraction by weight in the liquid, and y in the vapor, the numerical value of alpha remaining unchanged.

From p. 586 it is seen that the vapor composition for partially miscible liquids, the limits of miscibility of which are known, can be calculated by assuming Raoult's law for the component present in large amount and Henry's law to hold for the other component.

The great majority of mixtures of liquids miscible in all proportions do not follow Raoult's law even approximately, and hence the vapor compositions must be determined experimentally.[1] This may be conveniently done by boiling the liquid mixture and analyzing the vapors given off from it. Experimental results show that the vapor evolved from such a boiling liquid is in equilibrium with it as it escapes from the surface, due doubtless to perfect agitation incident to boiling. In this distillation, entrainment must be rigorously avoided on the one hand, and partial condensation at the top of the flask on the other. It is well to jacket the portion of the flask above the liquor line with hot gas, inasmuch as superheating does not change the composition of a vapor while partial condensation does.

With these precautions the experimental determination of vapor composition is relatively easy. Certain difficulties in computation are introduced by the fact that the composition of the liquid is changing progressively throughout the distillation. These difficulties may be met by taking at any one time an amount of distillate so small that the change in liquid composition is essentially negligible. It is, however, safer to allow for the changes actually taking place by computing the results of the experiment according to methods developed on p. 598.

In this discussion the composition of both liquid and vapor will be expressed as either the weight per cent or the mol-fraction of the *lower* boiling constituent. (See page 599.) The percentage of this component in the liquid is called x, while the percentage of this same component in the vapor is called y. When in equilibrium, y is a definite function of x and can best be expressed graphically by what will be termed the x *vs.* y curve. For most liquid mixtures this x *vs.* y curve has been determined at atmos-

[1] However, see p. 584.

pheric pressure only; but fortunately the shape of this curve changes but little with either temperature or pressure.

The change of vapor composition with the change of boiling-point, together with other important characteristics of mixtures of ethyl alcohol and water are available and are shown in Fig. 145, where the abscissas are weight per cent of alcohol in the liquid mixture, and the ordinates corresponding with the individual curves and are placed directly on them.

Consider, for example, an aqueous solution containing 20 per cent of alcohol, which when heated at atmospheric pressure boils at 87° C. and evolves a vapor containing 67.6 per cent alcohol. If this liquid be heated under a vacuum such that it boils at 67° C., *i.e.*, 20° lower, the composition of the vapor evolved will be higher, as shown by the vapor composition correction curve. A liquid of this composition evolves a vapor 0.0436 per cent higher in alcohol for each degree under its boiling point at 760 mm. Therefore, at 67° C. the vapor composition will be 67.6+0.87 or 68.5 per cent alcohol.

The pressure under which a definite mixture will boil at any fixed temperature, may be calculated from the temperature of boiling under a pressure of 760 mm., by means of the ratio curve. Thus the 20 per cent alcohol mixture here considered is seen to exert a vapor pressure at its boiling point, 1.62 times that exerted by pure water at this temperature. Since the vapor pressure of water as read from the steam tables at 67° is 205 mm., the pressure under which this 20 per cent alcohol solution will boil at 67° is 1.62 times this value, or 332 mm. Since, however, this ratio curve changes somewhat with the temperature as shown by the correction formula on page 590, the absolute pressure here under consideration is found to be 333 mm.

The *x vs. y* curve of any known binary liquid mixture of components miscible in all proportions has a shape similar to one of the four types shown in Fig. 146. In this figure the vertical line at the left, corresponds to the pure, high boiling component *A*, while that at the right represents the low boiling substance *B*, numerical values referring in all cases to the weight per cent of *B* in the mixture. The vapor-composition curves of the first mixtures is the straight 45° line, curve 1, indicating that the vapor evolved from all possible mixtures has the same composition as the liquid from which it came. In this case no separation whatever by distillation is possible. Illustrations of this type are found in mixtures of stereoisomers. The second type, which may be described as the normal one, is represented by curve 2. In this case the vapor evolved from the liquid contains more of the low-boiling component than the liquid from which it came. An illustration is ammonia-water. In curve 3

are represented liquids which, when they contain small amounts of *B*, evolve a vapor richer in *B* than themselves, but when the amount of *B* in the liquid reaches a certain value the composition of the vapor becomes identical with that of the liquid, while beyond this point the liquid evolved vapor richer in the high boiling component *A* than themselves; that is, the volatility of the components is reversed. A familiar example is a mixture of ethyl alcohol and water, although curve 3 represents a mixture of alcohol and toluene. Curve 4 represents a mixture

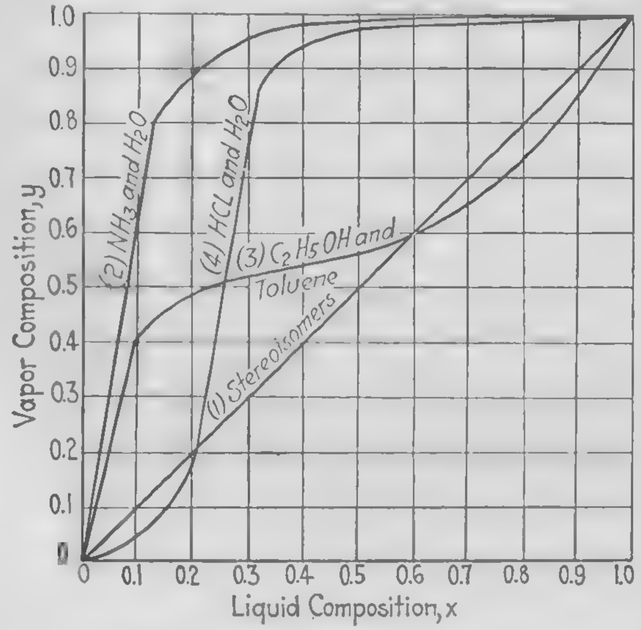


FIG. 146.—Typical *x vs. y* Curves.

in which a dilute solution of the low-boiling substance *B* evolves a larger percentage of *A* than it contains. In all solutions coming under this type a concentration of *B* is finally reached at which liquid and vapor compositions are equal, and beyond which the behavior of the mixtures is normal. Thus solutions of hydrochloric acid in water containing less than 20 per cent HCl, despite the fact that HCl boils 180° lower than water, evolve a vapor containing more water than themselves, although above this concentration the HCl behaves as the more volatile component. Those liquids having curves of type 3 possess *minimum boiling points* where the curves intersect the diagonal, while the

intersection of curves of type 4 with the diagonal represents liquids which possess *maximum boiling points.*

Complex Mixtures

In the case of more complex mixtures these relationships are extremely involved. Mixtures of hydrocarbons, the types and boiling points of which do not differ widely, usually follow Raoult's law within the experimental error. For other mixtures the vapor compositions must be determined experimentally. (See p. 591.)

Miscibility Complete, Volatility Normal.—In the distillation of completely miscible liquids of normal volatility in the mixture, the most volatile component tends to come over first.

With a rectifying column it is possible to take off the most volatile substance as distillate and to reflux all the other components down the column. But it is impossible to withdraw any other practically pure component from any particular point in the column, because on every plate in the column such a component will be contaminated with either the volatile distillate or the less volatile components of the residue, or both. All of the high-boiling components are therefore concentrated as a mixture in the still if operation is discontinuous or withdrawn from the bottom if continuous, *i.e.*, it is impossible to take more than one practically pure cut from a column still at one time. With continuous operation a second still and column can be employed to recover the product of next highest volatility, or with batch operation it can be distilled over after the most volatile component is out of the way. Thus in the distillation of light oil, benzene comes over first while toluene and xylene remain in the still; next the toluene is brought over, leaving the xylene and any higher-boiling components behind, and so on.

Petroleum.—In the distillation of petroleum the number of components in the mixture is very great and it is not usually desired to separate out the individual substances but rather mixtures of these within certain limits. From the preceding paragraph it is obvious that by proper rectification one may obtain a mixture of those components of lowest boiling point up to any desired point. From a second operation a second cut uncontaminated with both the first and with higher-boiling residues may be obtained, and so on.

Alcohol.—The behavior of fusel oil (amyl alcohol) in the distillation of the fermented mash in the manufacture of alcohol is interesting. The fusel oil boils at about 130° C., but is only sparingly soluble in water. Therefore as shown on p. 586, its volatility when dissolved in water is abnormally high. If in an alcohol column fusel oil gets down on the lower plates where there is practically nothing but water, its volatility is such that it is carried up the column. On the other hand any fusel oil which gets into the top of the column is in the zone of nearly pure alcohol. Here because of its complete miscibility its volatility is normal and hence, because of the high reflux, it is carried down again. It is obvious, therefore, that this component must concentrate in the middle of the column. In a batch operation it will remain in the middle until a large part of the alcohol is over and then it will distill with the low-test tailings. In a continuous column its concentration reaches such a point that it can be removed continuously from one of the plates in the middle of the column. The liquid removed contains both alcohol and water but the fusel oil has been concentrated to such an extent that its recovery from this liquid is easy.

METHODS OF CALCULATION

One Volatile Component: Steam Distillation

As was pointed out on page 566 many of the factors controlling the design of apparatus for steam distillation have already been considered. The method for calculating the composition of the vapor leaving the still, determining as it does the steam consumption, requires further consideration.

The equation

$$\frac{W_A}{W_B}=\frac{p_A M_A}{p_B M_B},$$

discussed on page 567, assumes the validity of the gas laws under the conditions obtaining. At atmospheric pressure deviations from these laws are generally not more than two or three per cent, and higher pressures are seldom used.

If the material distilled be entirely insoluble in water, p_A is the vapor pressure of the pure substance, and p_B is the difference between the pressure reigning in the system and p_A. Even

where mutual solubility is quite appreciable the equation may be employed, because since the vapor pressure of each is lowered approximately the same by the other, the ratio is but slightly affected.[1] Further, since the vapor-pressure curves of all substances are almost parallel, the ratio of the vapor pressures of two components change but little with temperature. When, however, the mutual solubility of the two substances is great, these considerations do not apply. In these cases one must estimate the partial pressures from the known solubilities as suggested on page 586.

Unless the steam used be highly superheated, or heat from an external source be supplied in addition to that of the steam, water will always be present in the still. This follows from the fact that when the heat of vaporization of the substance distilled is taken from the steam, an equivalent amount of water must be condensed.

In a direct-fired still operating by the semi-batch method, stearic acid is being purified by steam distillation in a vacuum. Superheated steam is injected into the mass by means of a system of perforated pipes in such a manner that the stearic acid vapors and steam leave the still at a temperature of 240° C., and the steam 70 per cent saturated with acid, *i.e.*, in a ratio equivalent to 70 per cent of the equilibrium value. Assume the following operating conditions to obtain: barometer, 748 mm. of mercury; vacuum in still, 662 mm., and temperature of material when charged, 70° F.

DATA

Average sp. ht. of solid stearic acid	0.4
Latent heat of fusion of stearic acid	47.6 gm. cal. per gm.
Melting point of stearic acid	64° C.
Average sp. ht. of liquid stearic acid	0.55
Latent heat of vaporization of acid at 240° C.	66.0 gm. cal. per gm.
Vapor pressure of stearic acid in mm. of mercury	
at 240° C.	19
at 220° C.	11
at 200° C.	3

Total heat above 70° F. of dry *saturated* steam at 240° C. = 1,233 B.t.u./lb. Sp. heat of low-pressure superheated steam = 0.46. Mol. wt. of acid = 284.4.

1. Calculate the pounds of acid passing to the condenser per pound of steam, on the assumption (*a*) that the top of the still is so jacketed by combustion products that no heat is lost by the vapors leaving the acid in the

[1] This is more strictly true when the molal solubilities of each in the other are approximately equal.

bottom of the still until they reach the condenser; (*b*) that the still is not thus jacketed and that the vapors cool 40° C. before leaving the top of the still; and, finally, (*c*) that the still is lagged but not jacketed, so that the vapors cool 20° before leaving the still.

2. In cases (*b*) and (*c*) what per cent of the acid initially evaporated in the still is refluxed back into it for re-evaporation, and what per cent of the total heat consumed in the initial distillation of the acid is lost by radiation and convection from the top of the still?

3. What is the total consumption of heat required for the distillation in the three cases, expressed as B.t.u. per lb. of product?

Basis: 1 lb. steam leaving the still at 240° C.

Pressure of acid = (0.70) (19) = 13.3 mm.
Total absolute pressure = 748 − 662 = 86 mm.
Pressure of steam = 86 − 13.3 = 72.7 mm.

Heat consumption in C.h.u. per lb. of acid:

To heat solid acid:	0.4 (64 − 21) =	17.2
To melt solid acid:	=	47.6
To heat liquid acid:	0.55 (240 − 64) =	96.9
To evaporate acid:	=	66.0
Total	=	227.7

Hence the heat used by the acid evaporated by 1 lb. of steam is 2.89 [1] times this in C.h.u. or 1.8 times the latter in B.t.u. = 1186. To this one must add the 1233 B.t.u. in the steam, or a total of 2419 B.t.u., which is 838 B.t.u. per lb. of product.

At 200° the weight of acid per lb. of steam (figured similarly to the above) is 0.57 lbs., *i.e.*, 2.32 lbs. are condensed and refluxed, or 80.3 per cent of the total evaporated. The heat lost is 1.8 (240 − 200) (0.46) = 33 B.t.u. due to cooling of the steam; 1.8 (240 − 200) (0.55) (0.57) = 23 B.t.u. due to cooling of acid vapor; 1.8 (66) (2.32) = 275 B.t.u. due to condensation; a total of 331 B.t.u. or 13.7 per cent of the total heat consumed.

Similarly, at 220°, the acid distilled per lb. of steam is 2.32 lbs., while the reflux is 0.575 lbs. or 19.9 per cent, and the heat lost is 131 B.t.u. or 5.4 per cent. Obviously, the heat consumption per pound of product is found by dividing the total used, 2419 B.t.u., by the yield. Hence the answers are as follows:

1*a*: 2.89 lbs. of acid evaporated per lb. of steam.
1*b*: 0.57 lbs. of acid evaporated per lb. of steam.
1*c*: 2.32 lbs. of acid evaporated per lb. of steam.
2*b*: 80.3 per cent of the acid is refluxed for 13.7 per cent heat loss.
2*c*: 19.9 per cent of the acid is refluxed for 5.4 per cent heat loss.
3*a*: 838 B.t.u. per lb. of product.
3*b*: 4240 B.t.u. per lb. of product.
3*c*: 1043 B.t.u. per lb. of product.

[1] (13.3) (284)/(72.7) (18.02) = 2.89 lbs. acid/lb. steam.

These figures strikingly illustrate the importance of avoiding loss of heat from the top of the still.

Miscible Binary Liquids

Simple Distillation, Rayleigh Equation.—The computation of the separation realizable in any given case of simple distillation was first made by Lord Rayleigh.[1] Since the composition of the liquid in a still will change continuously during distillation, the analysis must be a differential one.

Assume at any given time an amount of liquid in the still of weight L, the composition of which in respect to the more volatile component is x. Distil off the small amount dL, the composition of which will be y, where y is determined as a function of x by the x versus y equilibrium. Since in general y is greater than x, the composition of the liquid in respect to the more volatile component will now have fallen to a value of $x-dx$. The part left in the still is equal to the new concentration times the new weight $(x-dx)\ (L-dL)$, and that in the distillate will equal its concentration y, times the weight dL. These quantities may be equated, giving

$$xL=(x-dx)\ (L-dL)+ydL.$$

Or,

$$xL=xL-Ldx-xdL+dxdL+ydL.$$

Rejecting the second order differential, this becomes

$$\frac{dL}{L}=\frac{dx}{y-x},$$

which is the Rayleigh equation in the differential form. Integrating between the limits x_1 and x_2, with corresponding values L_1 and L_2

$$ln_e\frac{L_1}{L_2}=\int_{x_2}^{x_1}\frac{dx}{y-x}.$$

In the few cases where a mathematical relationship between x and y is known, this integral may be evaluated thereby, but as a usual thing resort must be had to the graphical determination of the area under the curve of $1/(y-x)$ versus x.

For the special case in which Raoult's law applies and in which, over the temperature range under consideration, the ratio of the pressure of the two components, P_1/P_2, is approximately constant, $y=\alpha x/[1+(\alpha-1)\ x]$ and this equation integrates to

$$ln_e\frac{L_1}{L_2}=\frac{1}{\alpha-1}\left\{ln_e\frac{x_1}{x_2}+\alpha ln_e\frac{1-x_2}{1-x_1}\right\},$$

where $\alpha=P_1/P_2$=relative volatility (see p. 579).

[1] *Phil. Mag.*, **1904**, 531.

For the special case of dilute solutions which follow Henry's law one may write $y=kx$, whence the integral becomes

$$ln_e\frac{L_1}{L_2}=\frac{1}{k-1}\ ln_e\frac{x_1}{x_2},$$

in which the units may be either mols or pounds.

Partial Condensation.—Theoretically there are two diametrically different ways of producing a partial condensation, that form two limiting cases between which all actual condensations lie. The first, which is called *simple condensation*, is characterized by keeping the condensate in contact and in equilibrium with the residual vapor, till the partial condensation is stopped. The second, *differential condensation*, consists in continually removing the condensate from the system as soon as formed. Continuous simple condensations may be perfectly and easily realized by maintaining a certain amount of liquid condensate in the condenser, bubbling the incoming vapors through the liquid with sufficient contact to secure equilibrium, producing the partial condensation by cooling the liquid itself, and removing the excess of liquid formed by a continuous overflow at the surface where the vapor escapes. There is no mechanical device to accomplish a perfect differential condensation, though it can be closely approximated.

Simple Partial Condensation.—Given a weight of vapor, G_1, of composition y_1, to be enriched by *simple* condensation to a composition of y_2, it is obvious that the condensate must have a composition x_2, connected with y_2 by the x versus y curve. Let the residual weight of vapor be G_2. Equating the original and final amounts of volatile component,

$$y_1G_1=y_2G_2+x_2(G_1-G_2),$$

or

$$G_2=G_1\frac{y_1-x_2}{y_2-x_2}.$$

Since neither G_2 nor the term y_2-x_2 can be negative, this equation loses its physical significance if x_2 be greater than y_1; in other words, the limit of enrichment of a vapor by simple condensation is represented by that vapor which is in equilibrium with the liquid having the composition of the original vapor, while the yield of enriched vapor is in this limiting case infinitesimal.

Differential Partial Condensation.—If the condensation be a *differential* one, the new concentration of the vapor is equal to the new amount of volatile component in the same, divided by its total weight, *i.e.*,

$$y+dy=\frac{yG+xdG}{G+dG},$$

whence,

$$yG+Gdy-xdG+dydG=yG-ydG.$$

Discarding the differential of the second order and solving,

$$\frac{dG}{G}=\frac{dy}{x-y},$$

whence

$$ln\frac{G_1}{G_2}=\int_{y_1}^{y_2}\frac{dy}{y-x}.$$

A differential condensation is more efficient than one, or any number of successive finite, simple, condensations between the same limits, and represents the theoretical maximum efficiency of separation. It may be considered as an infinite series of infinitesimal simple condensations. For purposes of comparison the performance of a partial condenser should be given in per cent of this theoretical maximum, which may be determined by measuring the area under the curve of $1/(y-x)$ versus y.

Rectification.—The mathematical theory of the rectifying column as applied to the distillation of binary mixtures was first developed by Ernst Sorel,[1] who calculated the enrichment from plate to plate by equating the amount of energy and of matter entering and leaving each plate and by assuming that equilibrium was realized between the vapors and the liquid through which it bubbled. Sorel applied his method successively from one plate to the next in a column. In consequence the computations become involved and it is difficult to visualize what is taking place. The following is a modification of Sorel's method, which simplifies computation and makes it possible to present results in graphical form.

The derivation will assume a column in continuous operation, with the feed, *i.e.*, the binary mixture to be separated, entering on a plate somewhere between the top and the bottom of the column. The results may, however, be applied to a discontinuous column at any particular instant during the operation, provided the amount of condensate in the column be small in proportion to the amount in the still.

Nomenclature.—The nomenclature is indicated by Fig. 147, where, for sake of simplicity, there is shown a single condenser, so that the overflow back into the column is of the same composition as the product. However, this has nothing to do with

[1] SOREL, "La Rectification de l'alcool," Paris, 1893.

the derivation and does not affect the validity of the equations. Heat is supplied by conduction at the bottom of the column, as by means of steam condensing in closed coils, or by externally firing the still.

Call any particular (variable) plate above the feed plate the nth and below it the mth plate. Call the amount of vapor, measured in mols per unit time, passing any particular section, V, and the amount of overflow passing the section, O. On the same basis, F, P, and W represent the respective amounts of feed, overhead product and residue. These quantities are to

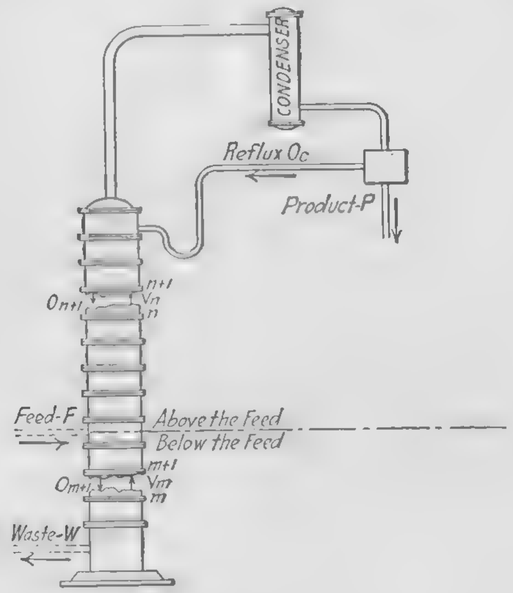


FIG. 147.

include in each case the mols of both components. Designate the point of origin of the particular vapor or overflow referred to by the use of a subscript; thus, V_n is the mols of vapor rising from the nth plate, while O_{n+1} is the mols of overflow coming down to that plate from the plate above. Use the subscripts f and c to refer to the feed line and to the condenser, respectively. Call the mol fraction of the more volatile component in the liquid x and the mol fraction in the vapor y. Indicate the liquid to which reference is made by subscripts; thus x_w is the mol fraction of volatile component in the residue leaving the bottom of the still, while y_m is the mol fraction of the same component

in the vapor rising from the mth plate. The quantities required in discussion are assembled in the following table:

x = Mol fraction of more volatile component in liquid.
y = Mol fraction of more volatile component in vapor.
P = Mols of distillate withdrawn as product per unit of time.
x_c = Mol fraction of more volatile component in the distillate.
O_{n+1} = Mols of overflow from plate $n+1$ to plate n, per unit time.
x_{n+1} = Mol fraction of more volatile component in overflow, O_{n+1}.
V_n = Mols of vapor passing from plate n to plate $n+1$ per unit time.
y_n = Mol fraction of more volatile component in vapor, V_n.
F = Mols of the mixture fed to the column per unit time.
x_f = Mol fraction of more volatile component in feed, F.
W = Mols of residue per unit time.
x_w = Mol fraction of more volatile component in residue, W.
O'_{n+1} = Theoretical minimum overflow from plate $n+1$, per unit time.
k = Average fractionation efficiency of the tower and plates, *i.e.*, ratio of the number of plates theoretically required to the actual requirement.
n = The number of the plate under consideration, counting from the feed plate up.
m = The number of the plate under consideration, below the feed plate, counting up from the still.
Q_n = *Total* latent heat in the vapor V_n.
r_1 = Molal heat of vaporization of more volatile component.
r_2 = Molal heat of vaporization of less volatile component.

It is easy to visualize each step and appreciate its significance by discussion of a special, illustrative case; consequently the following will refer to the separation of alcohol and water, alcohol being the more volatile component.

Consider the whole apparatus above a section drawn between the nth and the $(n+1)$th plate just below the latter. The only thing entering this section is the vapor from the nth plate, V_n. Leaving this section is the product P, and the overflow from the $(n+1)$th plate, O_{n+1}. Therefore, by a total material balance,

$$V_n = O_{n+1} + P. \quad \ldots \quad (1)$$

The total alcohol entering this section must equal that leaving it, *i.e.*,

$$y_n V_n = x_{n+1} O_{n+1} + x_c P. \quad \ldots \quad (2)$$

By eliminating V_n from these two equations, one obtains

$$y_n = \frac{O_{n+1} x_{n+1}}{O_{n+1} + P} + \frac{P x_c}{O_{n+1} + P}. \quad \ldots \quad (3)$$

Similarly, for conditions below the feed plate one obtains,

$$y_m = \frac{O_{m+1}\, x_{m+1}}{O_{m+1} - W} - \frac{W x_w}{O_{m+1} - W} \quad \ldots \quad (4)$$

Since these equations represent nothing but equality of input and output, for conditions of steady operation their validity cannot be questioned. Furthermore, inspection of Eq. (3) shows that under these conditions, it contains only three variables, x_{n+1}, y_n, and O_{n+1}. Similarly, the only variables in Eq. (4) are x_{m+1}, y_m, and O_{m+1}. Obviously, therefore, one needs to find only one other independent relationship between these variables to determine the value of both the others if that of any one be known at any point in the column, and this relation is a heat balance. While the principle underlying such a heat balance is simple, its details become, in the general case, sufficiently involved to interfere with a clean-cut visualization of the significance of the results. Hence, to avoid this difficulty, at the start certain simplifying assumptions will be made, which, as it happens, are, none the less, in many important cases close approximations to the facts.

The heat supply to that part of the column above the nth plate is obviously restricted to the heat content of the vapor V_n entering it. Part of this heat may be lost through the walls, part is consumed in heating up the liquid overflow going down the column, and the rest goes to supply the heat in the vapor rising to the plates above. Since heat loss by conduction through and radiation from the walls of the column should be eliminated, so far as practicable, by lagging or otherwise, it will now be assumed that this has been done to a point such that heat thus lost is a negligible fraction of the total.[1] Furthermore, where the specific heats of the components are small compared with the latent heats and where the temperature gradient through the

[1] Where a column is large in cross-section and operated to its full vapor capacity, the ratio of surface to volume becomes so small that heat losses from the sides are sometimes a negligible fraction of the total, so far as these calculations are concerned, even though the column be uninsulated and the losses large in absolute value.

column is small (*i.e.*, where the difference in boiling points between distillate and residue is not great), that fraction of the total heat which goes to heat up the overflow on its way down the column[1] may be negligible. That such is the case will be the *second* assumption made. The heat of mixing of liquids which do not react chemically or exhibit the phenomena of dissociation, molecular association, and the like, is usually small, particularly in comparison with the latent heats of vaporization. The heat of mixing of the vapors is even smaller. The *third* assumption will be that these factors are not appreciable. From these assumptions it follows that the latent heat of the vapor passing any given section of the column above the feed plate is found as latent heat in the vapor at any other section higher up, *i.e.*, that the total latent heat of the vapor at all sections above the feed plate is a constant quantity for fixed conditions of continuous operation. An analogous argument will demonstrate a similar rule below the feed plate and, if the feed enters at its boiling point, the latent heat has the same constant value throughout the entire column. If the feed enters below its boiling point, excess vapor must rise through the lower part of the column to warm the feed to the boiling point.

Liquids can be divided into two groups, the associating and non-associating types. Within each group the molal heat of vaporization divided by the absolute temperature is substantially constant, provided the boiling temperatures are not far distant from each other (Trouton's rule, p. 14). Since distillation is a serious problem only where the boiling points of the components are nearly the same, this is equivalent to saying that the molal heats of vaporization of the components in the column will usually be practically equal if both components be associating (water, ammonia, alcohol, etc.), or if both be non-associating (hydrocarbons and most organic liquids). Finally, it is assumed that the two liquids in the column belong to the same group, *i.e.*, that the molal heats of vaporization are nearly the same. On this basis, it is obvious that for each mol of high-boiling constituents condensed out of the vapor, a mol of low-boiling constituent must be volatilized from the liquid. In other words, above the feed

[1] It must be remembered that in the column the liquid on each plate must be at its boiling point, since otherwise it would not evolve vapor to pass on up the column.

plate, both the molal overflow from plate to plate and the mols of vapor passing up the column must be constant throughout this section; the same applies below the feed plate but the vapor will, however, obviously be greater than above the feed plate if the feed enters below its boiling point, since some vapor must condense to heat the feed. In all cases the overflow is greater below the feed plate than above it, as a result of the amount of liquid mixture fed into the column. Since it is impossible to condense the vapor from the top plate without cooling it below its boiling point, the reflux from the condenser will be cooler than the boiling liquid on the top plate; hence the amount of overflow in the column is greater than the reflux from the condenser. The effect of this is often negligible but may be large.

Under such conditions, therefore, the molal overflow from plate to plate above the feed plate, *i.e.*, the term O_{n+1} in Eq. (3) is constant and, similarly O_{m+1} in Eq. (4), however, O_{m+1} is greater than O_{n+1}. Hence, it follows that x_{n+1} is linear in y_n and x_{m+1} in y_m.[1] Furthermore, for fixed operating conditions, *i.e.*, definite quantities and concentrations of feed, distillate and residue and a given overflow, the slopes of these lines are known and the location of a single point upon either of them determines the whole line. Since these lines, based as they are only upon energy and material balances in the column, represent the conditions necessarily existing at each section in the column between the vapor rising and the overflow passing down through that section, they are called the operating or rectifying lines. To distinguish between conditions above and below the feed plate, the former may, in any specific case, be called the enriching and the latter the exhausting line.

It must be emphasized that, so far as a bubble plate column is concerned, the preceding discussion has been limited to the relation between the composition of the vapor rising from a plate and that of the overflow onto it from the plate above. The relation between the composition of the vapor and that of the liquid on the plate below from which it came must now be considered.

All available data indicate that the vapor evolved from any mixture of volatile liquids is, at the moment of its evolution, in complete equilibrium with the liquid from which it is given off. The vapor rising from a given plate of a column is, however, by no

[1] McCabe and Thiele, Graphical Design of Fractionating Columns, Ind. Eng. Chem., **17** (June, 1925), 605.

means all evolved from the liquid on that plate; it consists largely of vapor from lower plates, which because of inadequate contact with the liquid on the plate in question, has not had opportunity completely to react and come into equilibrium with it. Furthermore, the liquid on a plate is not uniform in composition but grows progressively poorer in volatile constituent as it flows from the point of discharge of the overflow from the plate above, across the plate, to the entrance to the overflow pipe leading to the plate below. It must, however, be kept in mind that the violent agitation produced by the vapor rising beneath the surface of the liquid tends to give thorough mixing and hence to maintain substantial uniformity of liquid composition on each plate. Such perfect mixing is usually assumed as the basis of column design. This obviously implies that the composition of the overflow onto the plate below is identical with that of the reacting liquid on the plate from which it comes. In an ideal column, perfect vapor-liquid contact would give a result equivalent to complete condensation of the vapor rising into a plate in the liquid on it, the heat of this condensation serving to evolve a new vapor in equilibrium with it (see p. 563). Such an ideal column serves as the standard of performance of rectifying equipment. In it the relation between the composition of the vapor at a given section and that of the liquid on the plate from which that vapor came must, therefore, be given by the equilibrium x-y curve.

It follows, therefore, that the conditions existing in a column operating continuously, with a constant value of the molal overflow above the feed plate and another, larger, constant overflow below it, in which the vapor rising from each plate is in substantial equilibrium with the liquid of uniform composition on that plate, may be represented by a diagram similar to Fig. 148. Equilibrium is represented by the curve *OEFG*. The operating lines are *AB* and *DF*, corresponding to Eqs. (3) and (4), respectively. Consider, for the moment, a plate on which the composition of the liquid is x_2. Since the vapor rising from this plate is in equilibrium with this liquid, its composition must be y_2, corresponding to a point L on the equilibrium curve. Furthermore, the composition of the vapor rising from the plate below must be y_3, determined by the point S vertically below L, since the relation between the composition of the vapor rising into a plate and that of the overflow from it (identical with that of the liquid on it) is given by the

enriching line AB. Similarly, the composition of the liquid on the plate above the one in question must be x_1; *i.e.*, the abscissa of that point R on the enriching line which has the same vapor composition y_2 as point L, and therefore lies on the same horizontal level with it. In other words, the changes in concentration, as one goes from plate to plate down the column, are found quantitatively by going stepwise alternately from the enriching line to the equilibrium curve and back again, first horizontally

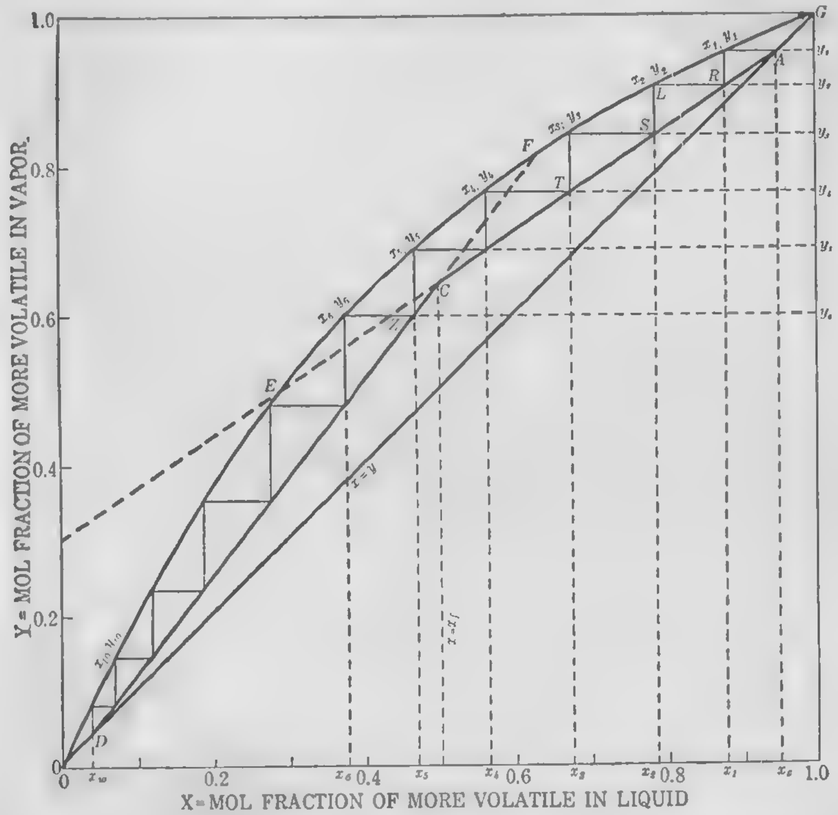


FIG. 148.—Diagram Illustrating Graphical Stepwise Method of McCabe and Thiele.

and then vertically, as indicated in Fig. 148. Thus, if x_1 is the composition of the liquid on one plate, x_2 is that on the plate below, x_3 on the next, and so on.

To start this stepwise operation, one must know the composition of the liquid on some one plate or else that of the vapor from it. In the case of the arrangement of Fig. 147, inspection

makes it clear that the composition of the vapor from the top plate must be identical with that of the product x_c, since no separation or enrichment of this vapor takes place in the condenser. Calling the top plate liquor composition x_1, and the corresponding vapor y_1, it follows that $y_1=x_c$. Hence x_1 is found by going vertically at the abscissa, $x=x_c$, to the 45-deg. line *ODAG* (along which obviously $x=y$), thus fixing the point A. x_1 is on the equilibrium curve, horizontally to the left of A.

Furthermore, if in Eq. (3) one insert top plate conditions for this case, namely, $y_n=x_c$, one obtains $x_{n+1}=y_n=x_c$; in other words, the enrichment line must go through point A, as above determined. Rearranging[1] Eqs. (3) and (4)

$$y_n=\frac{O_{n+1}}{V_n}x_{n+1}+\frac{Px_c}{V_n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

and

$$y_m=\frac{O_{m+1}}{V_m}x_{m+1}-\frac{Wx_w}{V_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

it is obvious that the ratio of reflux to vapor, O_{n+1}/V_n, is the slope of the enrichment line. Hence, when this ratio is known, the line AB is fully determined and readily drawn. Therefore, for the conditions in question the following rule may be formulated. On the x-y diagram plot the equilibrium curve *OEFG* and the diagonal *ODAG*. Determine point A corresponding to the abscissa $x=x_c$. Draw the line AB with the slope O_{n+1}/V_n. Conditions from plate to plate in the column are determined by going from point A horizontally to the equilibrium curve, then vertically down to the operating enrichment line AB, and so on.

If in Eq. (4a) one will let $x_{m+1}=x_w$, one finds that $x_{m+1}=y_m=x_w$; *i.e.*, the exhausting line must of necessity go through the point D, on the diagonal *ODAG*, corresponding to the abscissa $x=x_w$. Furthermore, its slope is O_{m+1}/V_m, though this slope is normally numerically larger than above the feed plate. In any case, this line DF is determined by the operating conditions and readily drawn. In the stepwise determination of plate-to-

[1] Equation (3a) may also be obtained *directly* from Eq. (2), which represents equality of input to output of the more volatile component in the section above the feed plate. Equation (4a) is a similar balance on the section below the feed plate.

plate conditions below the point of feed, this operating line must be employed instead of the line AB.

In going down the column along the enrichment line, one must face the question as to where it is necessary or desirable to change to the exhausting line, *i.e.*, on what plate in the column should the feed be introduced. It is obvious that at every point the vapor will be poorer in low-boiling constituent than corresponds to equilibrium with the liquid at the same section of the column; in other words, operating conditions in the column can never correspond to any point to the left of the equilibrium curve. Obviously, therefore, the enriching line loses its physical significance below the point E and the exhausting line above the point F. The composition of the liquid on the feed plate, however, can never exceed that of the feed, and consequently there can be no operating point on the exhausting line above the point C.[1]

Inspection of Fig. 148 shows that point z corresponds to the conditions on the highest plate that can possibly be the feed plate. Inspection likewise shows that one might follow the enriching line further down than this, but as each step corre-

[1] This can be made clear by the following analysis. Consider a column operating continuously with constant rates and compositions of feed, distillate, and residue, and constant supply of heat at the bottom and removal at the top. Assume that the valve in the feed line be suddenly closed. It is clear that the concentrations at all points in the column will start to drop. It is true that there will be a certain time lag in this effect; that, for example, concentration changes at the top will not develop until vapor from the feed plate has penetrated up the column; none the less, concentrations will fall and this drop will start first at the feed plate. Obviously, therefore, in normal continuous operation concentrations are held up to the operating values because of the introduction of low-boiling material in the feed. This means that the boiling liquid on the feed plate is subjected to a combination of effects, the net overall result of which, except for the introduction of the feed, is to reduce its concentration, and this reduction in concentration of the liquor on the feed plate is prevented by the influx of the feed. Were the composition of the liquid on the feed plate richer than that of the feed, the introduction of the latter would obviously tend to dilute the former, not to maintain its concentration. Therefore it follows that the composition of the liquid on the feed plate must be lower than that of the feed, though the concentration difference between the two may in the limiting case be only a differential amount. Hence, the composition of the liquid on the feed plate must be below point C of Fig. 148, corresponding to the abscissa $x=x_f$.

sponds to a plate, it is obvious that to do so would be to necessitate the use of a larger number of plates for the operation as a whole than is required by changing from the enriching line to the exhausting line at the earliest possible moment. In other words, while the feed can be introduced into the column at any point below the point C and above E in Fig. 148, it will shorten the column, and therefore reduce construction expense with no counterbalancing disadvantages whatsoever to introduce it, *i.e.*, to shift from the enriching line to the exhausting line, at the highest possible point below C.

In the ideal column the final step must of necessity fall on point D, corresponding to the composition of the effluent liquid in the still. If, on the diagram as constructed, this does not happen it means that, from the point of view of material and heat balances, the column cannot operate to meet all the conditions set. Thus, to look at it in one way, the overflow chosen is incompatible with the separation assumed. The choice of a slightly different overflow, however, will change the slopes of the operating lines, AC and DC, and a very slight shift in these will make the last step fall at D. It is not usual, however, to make such an adjustment, because if one sees to it that the last step overlaps the point D, one is on the safe side. In other words, an ideal column with these many steps would give the separation required with a trifle smaller overflow.

From an overall heat balance, it is obvious that, if the feed enters as liquid at the boiling point, in the ideal column the molal overflow below the feed plate will equal the mols of feed plus the overflow from the enriching section, and the intersection of the enriching and exhausting lines, *i.e.*, the point C, must of necessity fall on the vertical line the abscissa of which corresponds to the concentration of the feed, *i.e.*, at $x=x_f$.

Inspection will show that the steeper the operating lines, *viz.*, the larger the ratio of reflux to vapor, the smaller the number of steps and therefore the less the necessary length of the column. Since reflux is obtained, however, particularly that in the upper part of the column, by boiling vapor out of the still and condensing it at the top, not to be taken off as distillate, but to be returned down the tower, it is obvious that steepness of the operating lines and resulting saving in column height is

obtained by increased heat consumption. Heat can be saved by using less reflux, flatter lines, and a longer column.

Theoretically Minimum Reflux Ratio.—Since, however, operating concentrations cannot exist to the left of the equilibrium curve, inspection of Fig. 149 makes it clear that any such lines as da and ae are inoperable and that the flattest lines which are operable are represented by the combination db and be. For

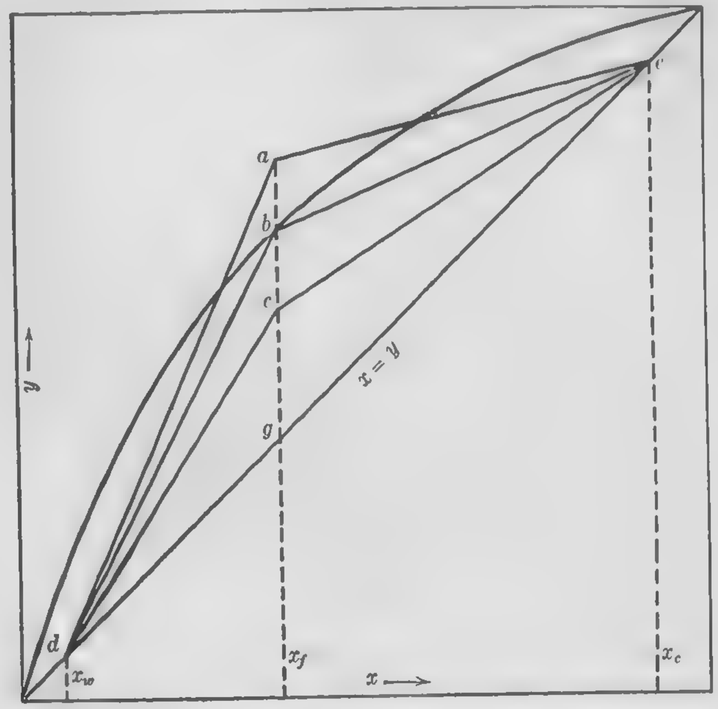


FIG. 149.

this case, however, it will be clear that in drawing in the steps corresponding to successive plate conditions, at the point b one will encounter an *infinite* number of indefinitely small steps on both the enriching and exhausting lines. In other words, this would involve a column of infinite height. The reflux ratio corresponding to this line will be called the minimum reflux ratio. When the liquid feed is at the boiling point, the minimum reflux ratio is given by the equation:

$$\frac{O'_{n+1}}{V_n} = \frac{x_c - y_n}{x_c - x_n} \quad \ldots\ldots\ldots \quad (5)$$

Also since $V_n = O'_{n+1} + P$,

$$\frac{O'_{n+1}}{P} = \frac{x_c - y_n}{y_n - x_n} \quad \ldots\ldots\ldots\ldots\ldots (5a)$$

For liquids of normal volatility (see p. 584) the value of O'_{n+1}/V_n is greatest where y_n and x_n correspond to y_f and x_f, respectively. For liquids of abnormal relative volatility, such as alcohol-water, one could plot the line *db*, and from its slope, determine O'_{n+1}/V_n. Better precision, however, is obtained by calculating this value from Equations (5) or (5a), see pp. 616 and 619.

Actual operation will always correspond to a greater reflux and steeper lines than this, *i.e.*, to some such combinations as *dc* and *ce*.

Theoretically Minimum Number of Plates.—It is interesting to note that a reflux ratio of unity makes the operating lines coincide with the 45-deg. diagonal *dge*. This represents the smallest possible number of steps which will, under any conditions, give the required separation. Such a column has, however, a negligible capacity and an infinite heat consumption per unit product. It corresponds to the conditions of Figs. 133 to 135, discussed on pages 561 to 564.

Plate Efficiency.—In practice, equilibrium, between vapor and liquid is never reached. The number of plates theoretically necessary for a given enrichment, calculated from these equations, divided by the number actually required, is called the plate efficiency of the column. While this will obviously vary with operating conditions and character of construction, for all types of bubble plates the variation is remarkably small. Plate efficiencies higher than 80 per cent are apparently never realized. With good distribution of the vapor bubbles through the liquid, efficiencies are usually from 40 to 70 per cent. Some mixtures apparently give higher efficiencies than others and occasionally the concentration range in which one is operating seems to influence the result, although but little is known regarding these factors. Where operating conditions are unsatisfactory, however, efficiencies drop off sharply. Thus, if the bubble caps are so designed that the vapor bubbles are excessive in size, if the plates are not properly leveled so that most of the vapor goes through some of the caps and little or none through others, or if the overflow short-circuits across the plate without properly mixing with the liquid

on it, operating efficiencies as low as 20 to 25 per cent may be encountered. In the design and operation of the equipment, it is important to provide against such contingencies. The actual number of plates in the column is obtained by dividing the theoretical number, computed by the methods outlined above, by the plate efficiency which one can anticipate from the type of equipment and operating conditions it is proposed to employ.

Packed Columns.—Peters[1] has called attention to the fact that in the operation of packed towers a certain tower height is necessary to furnish the equivalent effect in separation of one theoretically perfect bubble plate.[2] He designates this as the height equivalent to one theoretical plate. This height is less the smaller the size of the packing material. For hollow cylindrical rings of length equal to diameter, Peters finds that 1-in. rings require 40 in. of tower height to furnish the equivalent of one theoretical plate, and that the height required for other sizes is substantially proportional to the size; *i.e.*, $\frac{1}{2}$-in. rings would require 20 in. of tower height, etc. A similar rule undoubtedly applies for other types of packing, but exact data are not available.

Illustration 2.—Let it be required to separate, by continuous rectification, a 50 mol-per cent mixture of benzene and toluene, leaving not to exceed 0.1 mol-per cent of benzene in the residue and the same amount of toluene in the distillate.

Since the relative volatility of benzene and toluene is normal, as shown on page 612, the theoretically minimum ratio of reflux to vapor may be determined by inserting in Eq. (5), $y_f = 0.713$ and $x_f = 0.500$, giving $O'_{n+1}/V_n = 0.573$, corresponding to $O'_{n+1}/P = 1.34$. Hence the ratio of reflux to vapor actually used must exceed 0.573, as otherwise an infinite number of plates would be required.

The corresponding diagram is shown in Fig. 150. The operating lines intersecting at point 3 correspond to a reflux ratio, $O_{n+1}/V_n = 0.767$. The number of perfect plates required, 19, is obtained by counting the steps drawn in for that case. The composition on the feed plate is 42 mol-per cent. It is obvious that one could employ a lower reflux ratio by using more plates. The operating lines intersecting at point 2 correspond to a reflux ratio of 0.667 and those meeting at point 1 to a ratio of 0.582. The last set of lines are based on a reflux ratio only slightly above the theoretical minimum value, 0.573. The second assumption requires 25 perfect plates and the third 41.

In Fig. 151 the compositions on each plate are plotted against the plate number for each of these three cases and smooth curves drawn through the points. The left-hand curve, corresponding to a large reflux, is S shaped,

[1] *Ind. Eng. Chem.*, **14**, No. 6 (June, 1922), 476.

[2] Computation methods for packed columns are given on pp. 675 to 715.

rising slowly at the bottom, much more rapidly in the middle of the column, and flattening off toward the top. This is characteristic of a rectification operation. In the right-hand curve, not only is the slope less at each concentration throughout the curve but there is a very decided flattening of the curve in the middle, corresponding to the pinching at the feed plate between

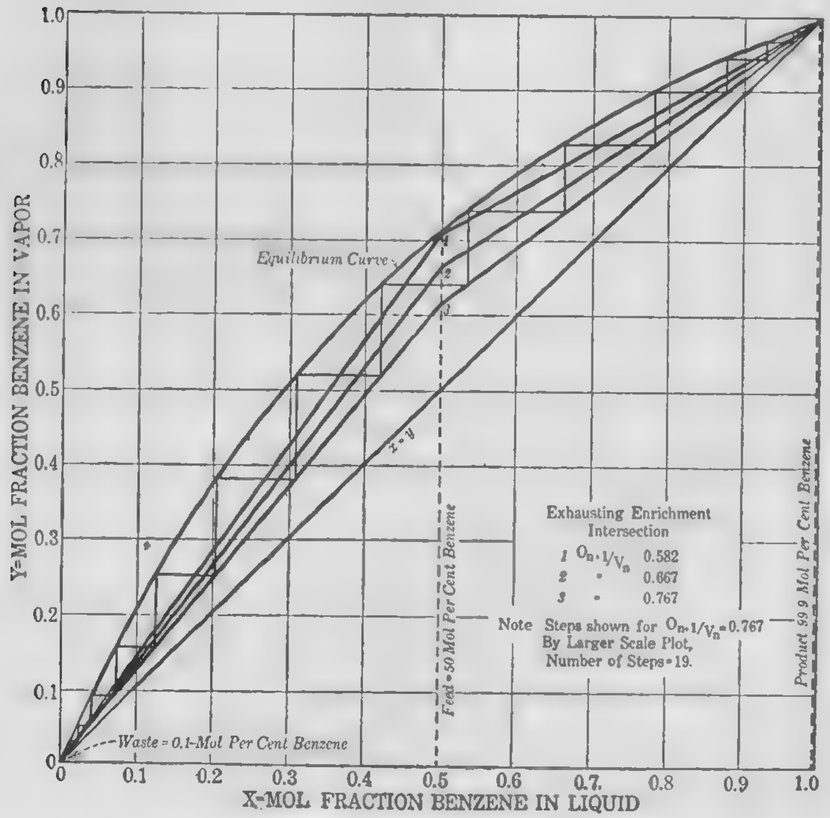

Y-MOL FRACTION BENZENE IN VAPOR
X-MOL FRACTION BENZENE IN LIQUID
Equilibrium Curve
x = y
Waste = 0.1-Mol Per Cent Benzene
Feed = 50 Mol Per Cent Benzene
Product 99.9 Mol Per Cent Benzene
Exhausting Enrichment
Intersection
1 On-1/Vn 0.582
2 " 0.667
3 " 0.767
Note Steps shown for On-1/Vn = 0.767
By Larger Scale Plot,
Number of Steps = 19.

FIG. 150.—Continuous Rectification of Benzene-Toluene in Ideal Bubble-Plate Column (Problem 2).

the operating lines and the equilibrium curve. Ordinarily, this phenomenon does not develop in operating columns because it is usually advisable to save on column size at the expense of a somewhat higher heat consumption corresponding to a higher reflux ratio. In the intermediate curve this flattening at the middle is barely detectable. The number of plates actually necessary for the separation will be found by dividing those shown on these diagrams by the plate efficiency.

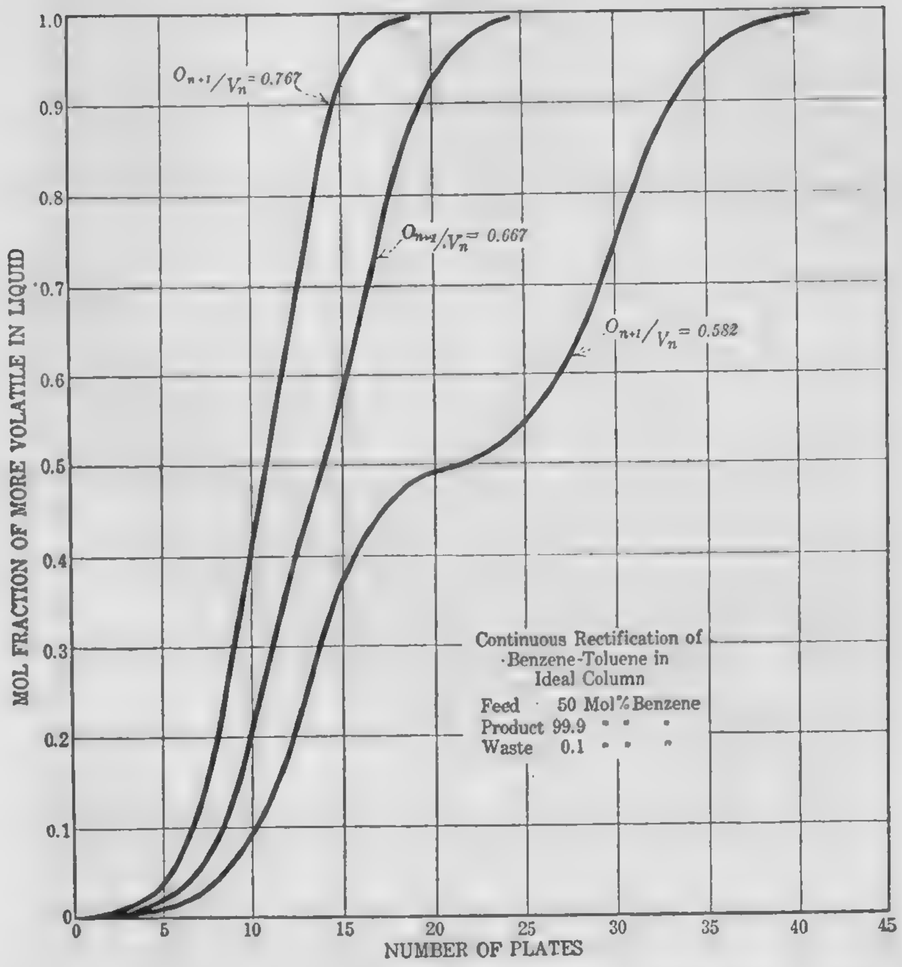


FIG. 151.—Concentration Gradients in the Ideal Bubble-Plate Column, Using Three Different Ratios of Reflux to Vapor.

Illustration 3.—It is desired to rectify continuously an aqueous solution containing 10 per cent alcohol by weight to produce a 94.5 per cent product and leave only 0.1 per cent alcohol in the residue, using the type of apparatus shown in Fig. 147.

What overflow should be used? What will be the height of the column required and at what point should the feed be introduced?

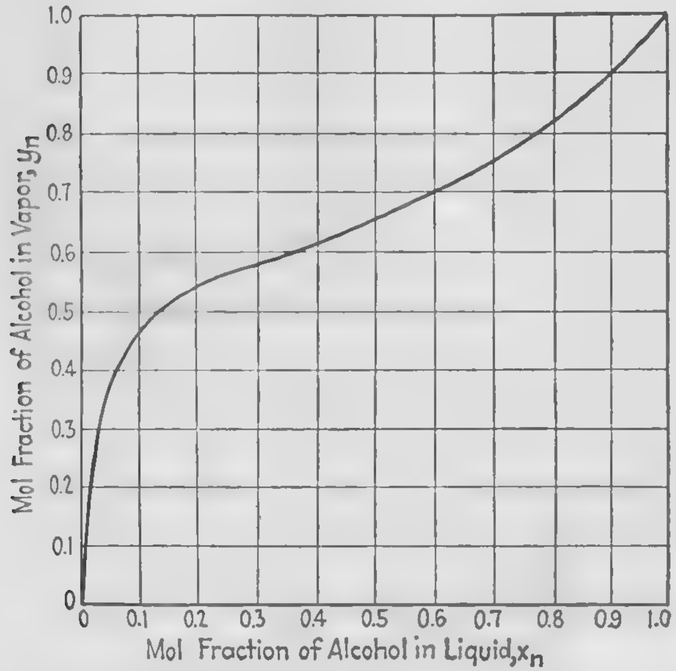


FIG. 152.—Curve of x vs. y for Alcohol-water Mixtures.

The mol fraction of alcohol in the feed is

$$\frac{\frac{10}{46.05}}{\frac{10}{46.05}+\frac{90}{18.02}}=0.0417,$$

that of the product similarly computed is 0.8705, and that of the waste 0.00039.

Figure 152 shows the equilibrium diagram for alcohol-water mixtures expressed in mol fraction of alcohol. Inspection of this diagram will show that if one attempt to draw an enrichment line from the point on the 45-deg. line corresponding to the composition of the product, 0.8705, to intersect the equilibrium curve at the composition of the feed, 0.0417, this line would cross the equilibrium curve in its upper end, slightly above $x=0.8$, and is, therefore, inoperable. The lowest operable ratio of reflux to vapor corresponds to a line starting at this same upper right-hand point and drawn tangent to the equilibrium curve. It is more exact, however, to determine

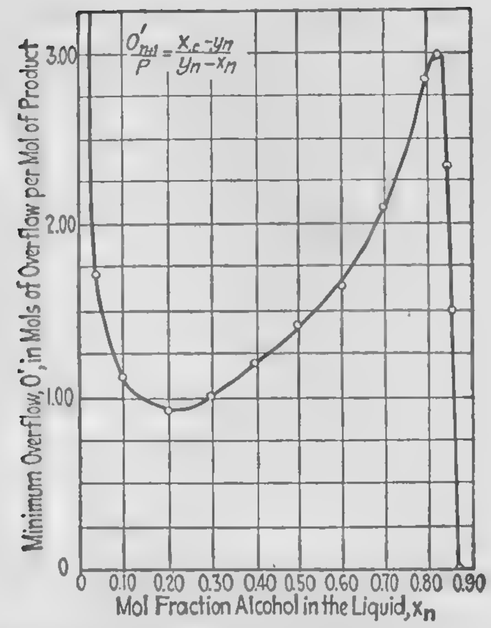


FIG. 153.—Variation of O' with x_n, for Rectification of Alcohol to 94.5 Per Cent by Weight (Problem 3, page 616).

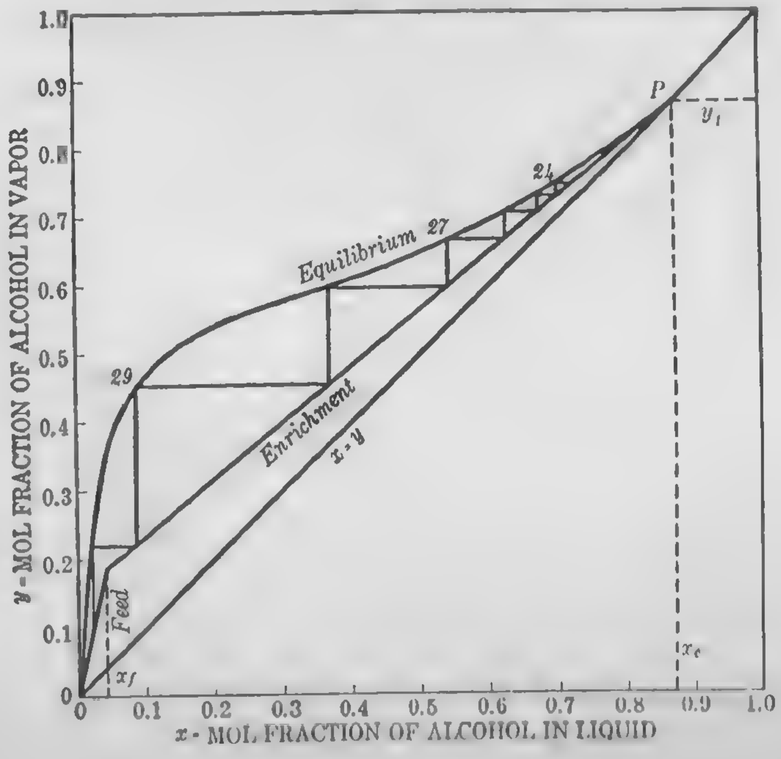


FIG. 154.—(Problem 3).

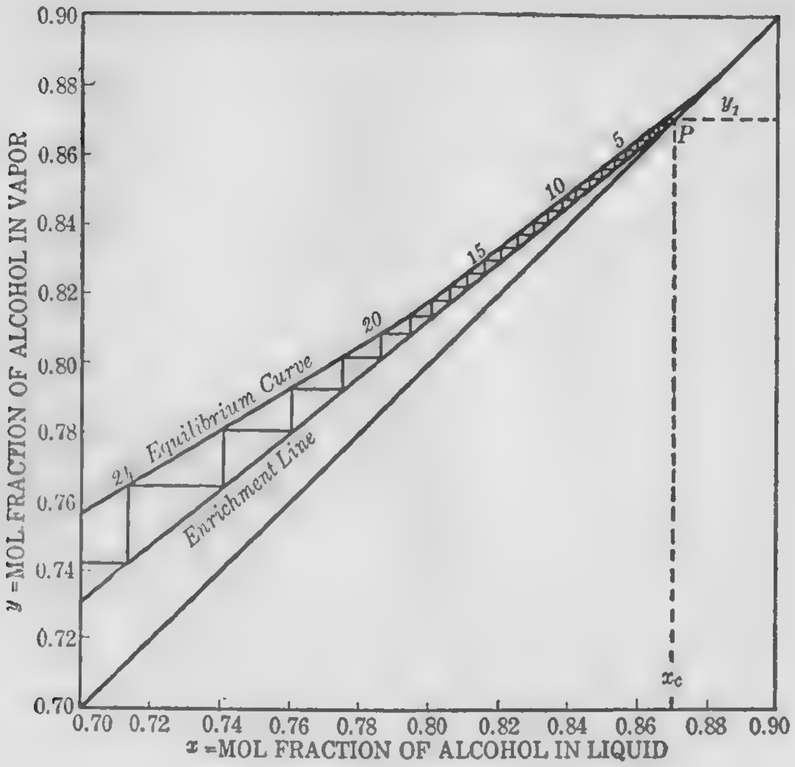


FIG. 155.—(Problem 3).

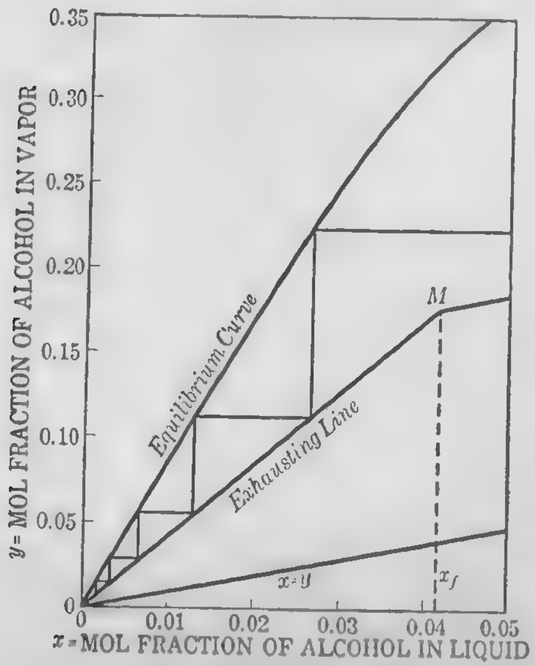


FIG. 156.—(Problem 3).

this reflux ratio by the use of Eq. (5*a*), substituting therein the values of x and y read from the equilibrium diagram. The results so obtained are plotted in Fig. 153 and indicate a minimum ratio of reflux to product of 3.[1] Since $V_n = O_{n+1} + P$, this corresponds to a ratio of reflux to vapor, O_{n+1}/V_n, of $\frac{3}{4}$. Such a ratio would, of course, call for a column of infinite height, and it is essential to increase the reflux ratio very materially because in this case the enriching line parallels the equilibrium curve so closely through a long range in the upper part of the diagram. It will be assumed that an operating ratio of reflux to product of 5 will be employed, corresponding to a ratio of reflux to vapor up the column of 0.833.

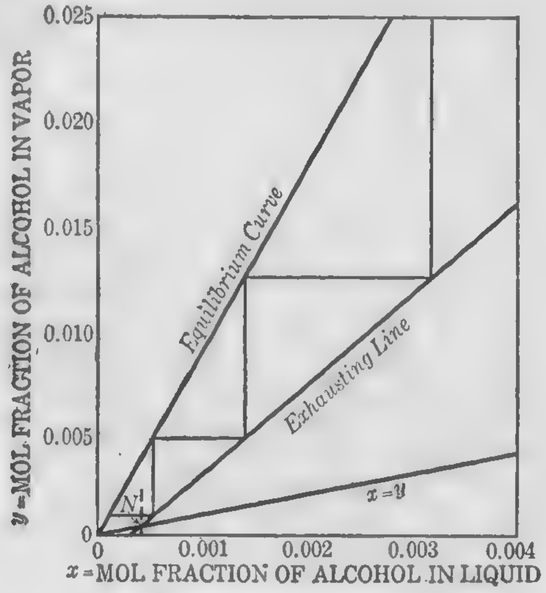


FIG. 157.—(Problem 3).

[1] Figure 153 shows that on the plate where $x_n = 0.835$ the theoretically minimum overflow must be 3.0 mols per mol of product. Between this point and the top plate, the theoretical overflow is smaller, and the same is true below $x_n = 0.835$ until the $x_n = 0.028$. At values lower than $x = 0.028$, it is seen that the theoretical overflow exceeds 3.0 mols per mol of product.

The minimum overflow below the feed plate is not shown, as calculation proves that any overflow sufficient above the feed plate, together with the feed itself, is more than the minimum overflow below the feed plate.

It must be kept in mind that every point on this curve is a minimum for that particular concentration. The lowest point on this curve is therefore a minimum of minima. The actual overflow in a column must be greater than the greatest value on this curve within the concentration limits between which rectification is being carried out.

The corresponding diagram is plotted in Fig. 154. Inspection shows that the enrichment line so nearly coincides with the equilibrium curve at the upper right-hand end that it is necessary greatly to enlarge this part of the diagram in order to secure precision. This is done in Fig. 155.

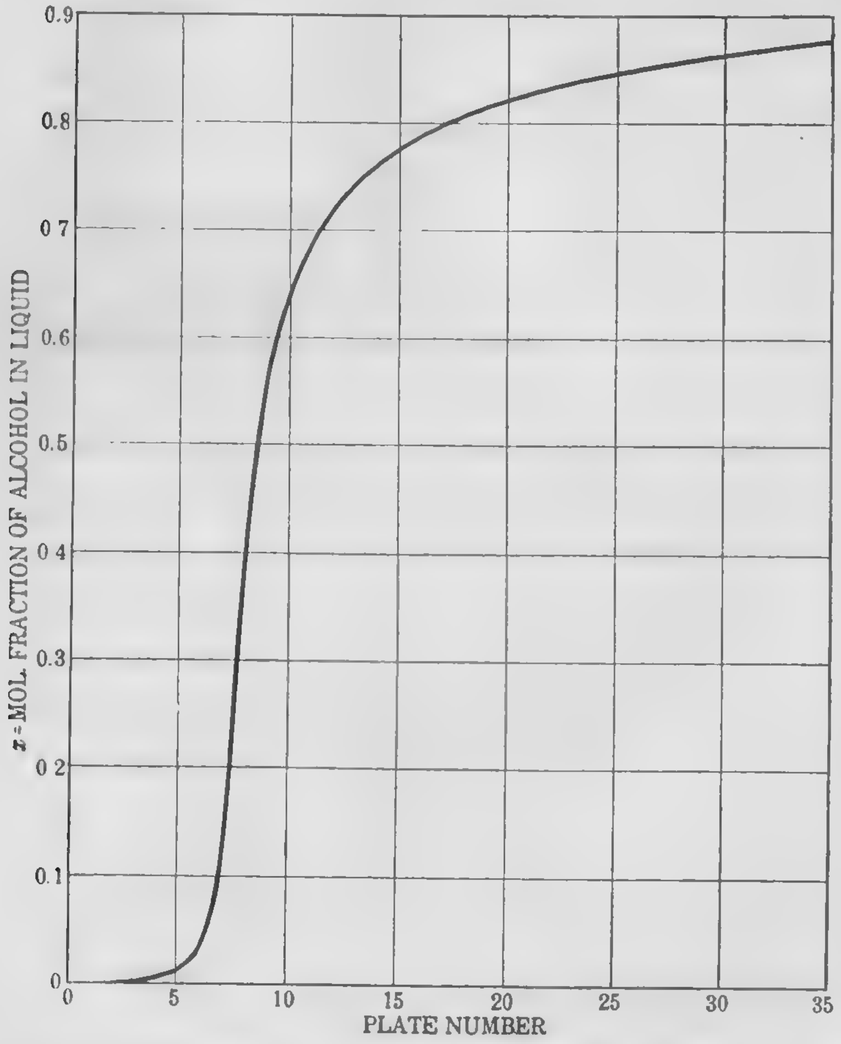


FIG. 158.—Concentration Gradient in Ideal Bubble-Plate Column for Separating Ethanol from Water (Problem 3).

Similar enlargement is necessary in the lower part of the diagram, as is shown in Fig. 156. Even this enlargement is inadequate for the lowest plates in the column and a still further enlargement is shown in Fig. 157. In the last two plots, for convenience, the scales of ordinates and abscissae differ.

The required number of perfect plates thus determined is 36, of which six are below the feed.

The concentration gradients in the alcohol column are shown in Fig. 158, and the S-shaped curve characteristic of rectifying operations is clearly apparent. Figure 159 is an enlargement of the lower part of Fig. 158.

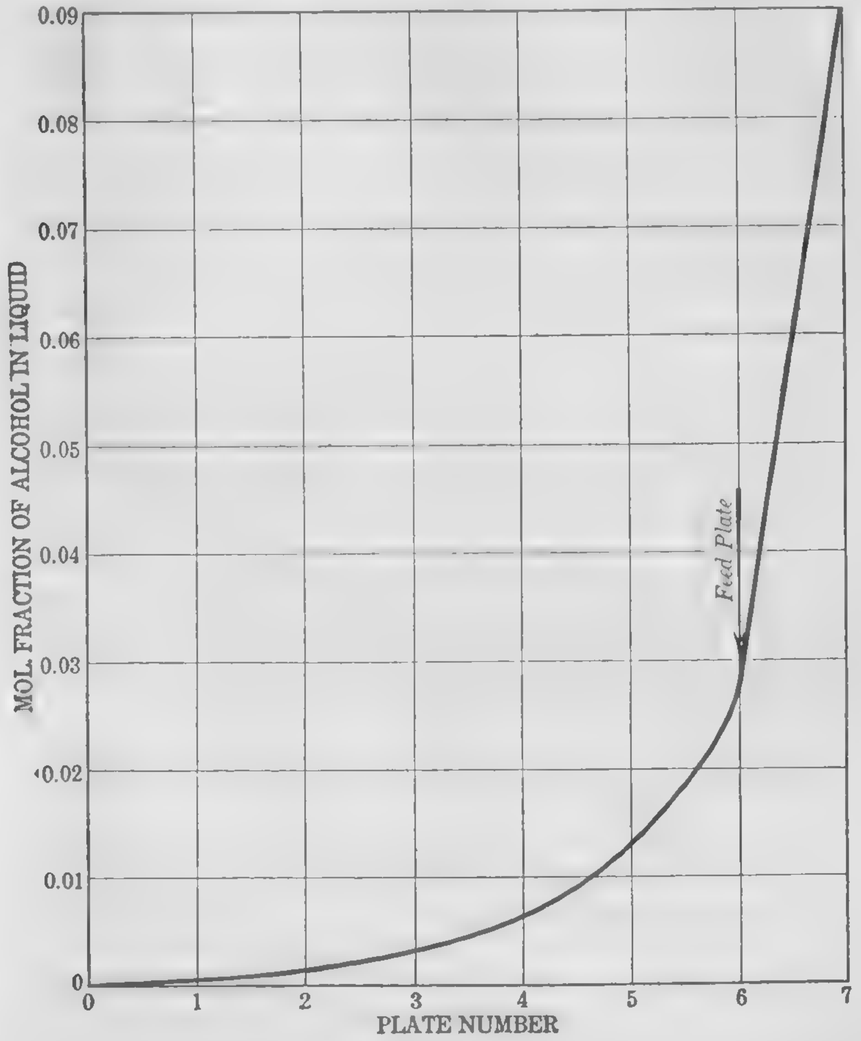


FIG. 159.—(Problem 3).

Attention should be called to the difference in the equilibrium diagrams between this case and that of benzene-toluene. The alcohol-water equilibrium curve approaches very closely to the 45-deg. line in the neighborhood of the constant-boiling mixture, whereas the benzene-toluene curve intersects the diagonal at $x = y = 1$ at a very considerable angle. This peculiarity in the alcohol-water diagram greatly lengthens the column and increases the necessary reflux ratio.

Figure 160 shows the influence, upon the number of perfect plates required in the column, of the amount of overflow, or, what is equivalent to the same thing, the heat consumption per unit amount of product. It has already been pointed out that in this particular case an overflow of at least 3 is required and this would involve a column of infinite height, *i.e.*, the curve is asympototic to an overflow of 3. An overflow of 4 requires 52 plates. An overflow of 6, however, reduces the plates to 30. An overflow of 20 requires 21 plates, and it is obvious that still larger overflows will save almost nothing in column construction. Intelligent design requires an economic balance between the cost of the column and that of the heat

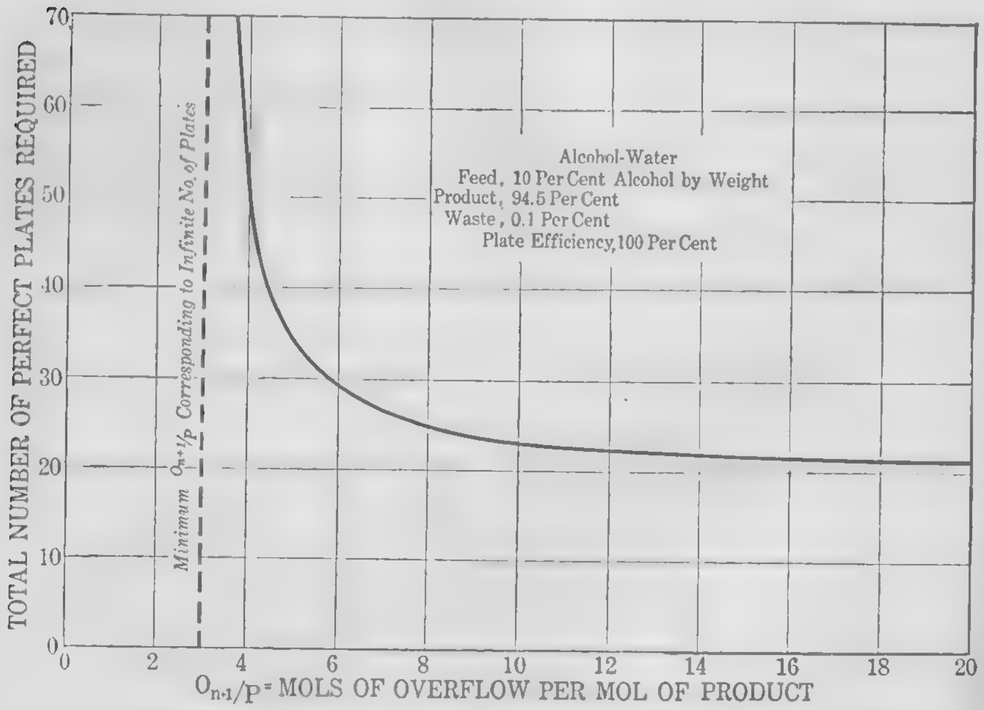


FIG. 160.—Relation between Ratio of Reflux to Vapor and Number of Perfect Plates. (See also page 626.)

required to operate it, and such a balance can immediately be struck from this curve once the cost of plates and of steam is given (see p. 626).

Equations for Unequal Molal Overflow.—As explained on page 603, the proof there given that the enrichment and exhausting lines are linear depended upon certain simplifying assumptions which it is now desirable to eliminate. It must, however, be kept in mind that Eqs. (3), (3*a*), (4), and (4*a*) depend only on

continuity of operation and are valid irrespective of any of the other assumptions made. The first case to consider is that in which the molal heats of vaporization of the two components of the mixture are different, but the other assumptions still apply. Calling the molal heats of vaporization of the two components r_1 and r_2 respectively, the total latent heat of the vapor rising from the nth plate is given by the expression,

$$Q_n = V_n[y_n r_1 + (1-y_n)r_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Furthermore, neglecting change in temperature of liquid and vapor from plate to plate and heat losses through the walls of the column, this quantity Q_n is constant at every section through the column above the feed plate. Combining this with Eq. (1), page 602, one obtains

$$O_{n+1} = \frac{Q_n}{[y_n r_1 + (1-y_n)r_2]} - P \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Inspection of this expression shows that in this case the overflow, instead of being constant, is a function of y_n. Insertion of any specific value of y_n in Eq. (7) gives the corresponding value of the overflow. Substitution of this value for O_{n+1}, along with the corresponding value of y_n in Eq. (3), gives the value of x_{n+1}, thereby determining a point on the enrichment curve. By assuming various values of y_n, one can thus determine any desired number of points on the enrichment curve. Plotting these determines the enrichment curve, which is then used in design in exactly the same manner as the enrichment line for constant molal overflow.[1] Below the feed plate, operating in an entirely analogous manner, one obtains the equation:

$$O_{m+1} = \frac{Q_m}{[y_m r_1 + (1-y_m)r_2]} + W \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Substituting any particular value of y_m in this equation, one obtains the value of O_{m+1} to be substituted in Eq. 4. The corresponding values of y_m and x_{m+1} determine a point on the exhausting or stripping curve.

Where the change in temperature through the column is not negligible, but the pressure drop is small, the temperature at any point is determined by the vapor composition (see the boiling-

[1] It should be noted that the values of y_n and x_n chosen need not correspond quantitatively to conditions at any specific plate; none the less they determine coordinates of the enrichment curve.

point curve such as shown in Fig. 145, p. 590). If now, as in the preceding paragraph, one assumes a value of y_n, the temperature of the vapor at the point in question is immediately determined, but the value of Q_n is greater than the total latent heat content of the vapors leaving the top of the column by an amount sufficient to heat the overflow from its temperature at the top of the column to its temperature at the section in question. This temperature of the overflow is unfortunately not determined until one knows the value of x_{n+1}. One can get an approximate value of x_{n+1} by neglecting this temperature correction and using the method of the preceding paragraph; then determine the corresponding temperature by the boiling point curve and repeat the process until the correct value of x_{n+1} is obtained by successive approximation. Thus, one can compute any required number of points on the enrichment curve and similarly below the feed plate.

Where pressure drop through the column and heat losses through the sides are appreciable, it is necessary to correct for these by similar methods. This requires a knowledge of the number of plates above the section in question. It is usually sufficient to estimate these particular corrections by making a preliminary determination of the number of plates by assuming constant molal overflow and then applying these corrections to the temperature of the vapor and the heat quantity Q_n as determined by the boiling-point curve, uncorrected for pressure drop.

It is entirely practicable to compute the concentration changes from plate to plate down the column, one plate at a time, by the use of these equations. Furthermore, where the total number of plates is small, *i.e.*, where the concentration changes per plate are large, this stepwise method is the shortest way of solving the problem except for the case of constant molal overflow. Where the number of plates is large, however, the graphical method is shorter because one needs to determine only a relatively small number of points on the operating lines as contrasted with the large number of computations necessary by the algebraic stepwise method. Furthermore, the graphical method possesses the decided advantage of offering an easy visualization of what is happening in the column which it is difficult or impossible to obtain by the algebraic method alone.

The above equations are derived on the assumption that the heat supplied to the bottom of the column is indirect. Particularly in those cases where water is the high-boiling component of the mixture, it is common practice to heat by blowing live steam into the still. It is obvious that in such cases the equations representing the material balances must be modified accordingly.

Vapor Velocity.—In designing columns the vapor velocities must be kept within reasonable limits to avoid undue friction; *i.e.*, vapor passages must be adequate. There must of course be sufficient pressure to overcome the liquid head on the plate and the friction through the vapor passages into the liquid. This latter is given by the orifice equation,[1] $u = c\sqrt{2gh}$, but the constant, c, of this equation is depressed by the presence of the liquid to a value of approximately 0.3. This excess pressure below the plate backs the liquid on the plate below up into the overflow pipe by a corresponding amount. The net distance between plates must be sufficient to provide for this pressure, as otherwise the liquid in the column will back up into the condenser.

There should be at least 6 inches between plates to allow for spattering and splashing, and even with this allowance entrainment of liquid into the plate above may be considerable. If the vapor velocity through the tower becomes too great this splashing will reach a point where the liquid is carried almost bodily into the plate above and from the top plate into the condenser. This effect is what limits the capacity of a column. It seems logical that this spattering should be determined by the vapor velocity where it enters the liquid, *i.e.*, by the volume of vapor per unit time per unit peripheral length of bell cap, but the inadequate data available indicate that it is determined rather by the superficial vapor velocity over the whole cross-section of the column. However, it is probably true, that if, owing to bubble caps of excessive size, there is a great deal of dead space in the column this allowable superficial velocity will be decreased. In well-designed bubble cap columns, operating under atmospheric pressure, the superficial vapor velocities allowable without excessive entrainment are[2] 1 to 1.3 ft. per sec. With similar

[1] u = average velocity through orifices in ft. per sec., h = friction through orifice, expressed in ft. of vapor, and g = the acceleration due to gravity or 32.2 ft. per sec. per sec.

[2] W. A. Peters, Jr., *J. Ind. Eng. Chem.*, 14, 476 (1922).

columns operated under high vacuum this figure rises to 4 to 5 ft. per second, and the same figures have been found for vacuum columns using baffle type fillings with no bubble caps. Perforated plates apparently allow higher vapor velocities, rising to 3 ft. per sec. This maximum allowable vapor velocity is to some degree dependent on the liquid mixture under treatment.

While the allowable linear velocity under a vacuum may be three to five times that at atmospheric pressure, the vapor densities at the pressures encountered under vacuum are less than one-tenth those at atmospheric pressure; hence the allowable mass velocity (p. 149) increases with pressure. Therefore, the capacity of a column of given diameter may be increased by operating under a pressure above atmospheric. As shown on pages 589 to 592, vapor composition does not change very rapidly with change in pressure. It follows that the operation of a rectifying column under pressure is advantageous because capacity is increased with little sacrifice of separation. This principle has for many years been successfully practiced in the separation of ammonia and water in absorption refrigeration machines.

It should be remembered that if the amount of reflux for a given product be increased in order that the number of plates in the column may be decreased, as suggested on page 622, two disadvantages are at the same time introduced. First, the heat consumption of the operation is proportionally increased, and second, the cross-section of the column must be enlarged to accommodate the greater volume of vapor which must rise through it.

It is important to provide adequate overflow pipes for the reflux, especially in those cases where the vapor quantity is small compared with the overflow, as in alcohol columns below the feed plate and the like. The capacity of these pipes is limited by the amount of liquid which can enter them, since this flows in under low head. The upper edge of the pipe acts as a weir, and the flow can be calculated by the Francis weir equation:

$$V = 3.33L(H)^{3/2},$$

where V = Cu. ft. per sec. discharged by each overflow pipe,
L = Perimeter of overflow pipe, in ft., and
H = Head on overflow pipe in ft., or maximum depth of liquid above edge of overflow pipe.

Since perimeter is the essential thing, rectangular or oval shapes are preferred, the width being approximately three times the height of the liquid above the upper edge.

There is in practice a certain amount of variation in the best depth of liquid on the plate. A depth of 6 inches has been employed but it seems better to restrict this depth to from 1 to 3 inches. When a bubble rises through the liquid the outside of the bubble soon comes to equilibrium, but the interior is protected by this saturated vapor film on the surface, and further interaction is slow. The bubble should therefore be broken up and reformed in order to mix the vapors, *i.e.*, the bubble should pass to the next plate.

Interdependence of Allowable Gas and Liquor Velocities.—Figure 161 shows a plot of liquor velocity *versus* allowable gas velocity, the latter being the velocity at which entrainment of liquid by vapor became marked. These results are based on the data of Peters,[1] obtained in packed towers operated at atmospheric pressure. Curve I of Fig. 161 shows results on water in a tower packed with $\frac{1}{4}$-in. hollow cylinders. As the liquor velocity down the column is increased, it is seen that the allowable gas velocity is reduced. According to these results, for this particular packing the maximum allowable liquor velocity is about 51 lb. per minute per square foot of total cross-section. The single point marked V was determined with the same packing but using alcohol in place of water. Due to the low liquor rate the allowable gas velocity is much higher. It will be seen that this point ties in well with the data of Curve I, probably because the allowable gas velocities were plotted as mass velocities rather than linear velocities.

Curve II shows the data for $\frac{1}{2}$-in. hollow cylinders, the curve being similar in shape to that of Curve I. At a given gas velocity, however, more liquor will flow down through the $\frac{1}{2}$-in. packing due to its larger size, and conversely for a given liquor velocity the allowable gas velocity is greater. Curve III shows results for $\frac{3}{4}$-in. copper nails and the curve is similar to Curve II. The one point for $\frac{1}{4}$-in. shot (IV) shows a low allowable velocity, as would be expected with the smaller free space. Data of this sort are most helpful in design; unfortunately, complete data are not available for the many types of tower fillings used commercially.

[1] W. A. Peters, Jr., *Loc. cit.*

Free Energy of Separation of Liquid Mixtures

The minimum work required to separate one mol of a mixture into its two volatile components under *reversible*, isothermal conditions is

$$W = RT\left[x ln_e \frac{P}{p} + (1-x) ln_e \frac{P'}{p'}\right]$$

where R is the gas constant, T is the absolute temperature, and x is the mol-

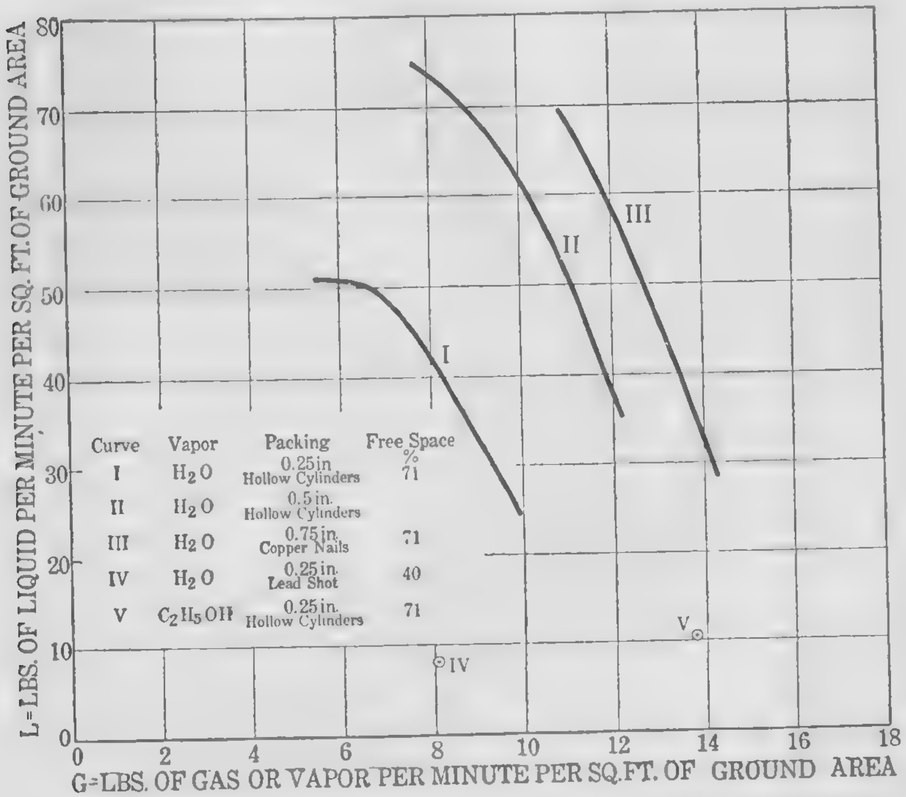


FIG. 161.—Allowable Velocities of Gas and Liquid in Packed Column for Rectification in Packed Column at Atmospheric Pressure.

fraction of the first component and $1-x$ of the second, p is the partial pressure of the first component in the mixture and P that of the same component in the pure state, while p' and P' apply similarly to the second component. This relation is not dependent upon Raoult's law but does assume that the vapors obey the gas laws. For mixtures which follow Raoult's law it simplifies to

$$W = -RT[x ln_e x + (1-x) ln_e (1-x)].$$

At any definite temperature this expression is independent of the pressures of the pure components, *i.e.*, the energy theoretically required to separate such

a mixture into its components is independent of their boiling points. On the other hand, this reversible work is seen to be proportional to the absolute temperature at which the separation is carried out. The minimum work of separation at 70° F. of an equi-molal mixture which follows Raoult's law is 730 B.t.u. Since in such a mixture the heat of vaporization of the low-boiling component alone is approximately 5200 B.t.u., it follows that distillation as ordinarily carried out is an extremely inefficient process. To secure high energy efficiency the heat employed should be (so far as possible) re-utilized, as is done for example in multiple effect evaporation. Furthermore, since separation by distillation is more difficult as the boiling points approach each other, one concludes that methods other than direct[1] distillation should, if possible, be employed for separating mixtures, the components of which boil close together, *i.e.*, distillation is not a reversible process.

[1] Thus methyl alcohol and acetone not only have boiling points which differ by less than nine degrees but form a constant boiling mixture. Their separation may, however, be effected by addition of some material very soluble in one but not in the other. Such a material will obviously lower the vapor pressure of the first but not the second. Caustic soda or potassium carbonate may be employed but tend to polymerize the acetone. Sodium thiosulphate is almost equally effective and does not have this disadvantage. If this substance be admitted into the top of a rectifying column, the methyl alcohol is effectively washed down the column while the acetone distills over. The thiosulphate is most conveniently added as a saturated aqueous solution and the methyl alcohol later freed from it by distillation. In problems of distillation modifications of this sort may be employed advantageously.

CHAPTER XVIII

GENERAL PRINCIPLES OF DIFFUSIONAL PROCESSES

PART I. CLASSIFICATION OF PROCESSES

When one faces the problem of separating a fluid mixture, gaseous or liquid, into its components, a number of methods of treatment are available (see pp. 334 to 335). For miscible liquids, distillation (see Chap. XVII) is usually but by no means always the best. The same method is applicable to mixed gases. Thus, in the manufacture of oxygen and nitrogen from air, one can liquify the whole mixture by compression coupled with refrigeration and separate the components by rectification. If one of the components of a gas has a high condensing temperature relative to the others, it is possible to condense it quite completely by compression and cooling or by refrigeration, or by combination of the two. The segregation of the components of gaseous mixtures by centrifugal action has been suggested, and selective diffusion through membranes has been employed. Frequently, one or more of the components can be removed by selective solubility in a suitable solvent or by combination, chemical or otherwise, with solid reagents. Of all these, however, the most important are selective absorption in liquids and adsorption on solids.[1]

[1] When a substance is taken up by a solid from a fluid (gas or liquid) selectively, *i.e.*, when at equilibrium it is possible to build up on the solid relatively high concentrations of the material at relatively low concentrations of it in the fluid phase, the phenomenon is ordinarily called *adsorption* (see p. 643). The term will be used consistently in this sense in the following chapters, independently of any interpretation as to the mechanism involved. Similar concentration relationships are sometimes found when a gas is dissolved by a liquid, as in the case of CO_2 in carbonate solutions (see p. 649), where, however, it is generally agreed that the mechanism is one of liquid solution. Furthermore, in the absorption of gases by solids, the concentration in the solid is sometimes proportional to the partial pressure of the gas, as, for example, in the absorption of various gases in rubber. The term *solution* is ordinarily used in such cases, but it is not certain that the mechanism is fundamentally different from that of adsorption. The term *absorption* will be used in a general sense and *adsorption* reserved for the special conditions indicated above.

All these processes last referred to involve the separation of mixtures of materials into their components by the introduction of a third material which will combine with one of the components preferentially to the other. Since in general the purpose of the operation is the recovery of the pure components, the material introduced should be readily separable from the component which it removes from the mixture. The cases falling under this classification are numerous and exceedingly diversified in detailed characteristics, but, because in all such separations both the underlying principles and the general methods of applying them are the same, these cases will be grouped together.

The mixture to be separated may be either solid, liquid or gas, and the same is true of the material added to effect separation. Corresponding to these cases there would therefore be the following nine possible combinations:

Case	Character of mixture undergoing treatment	Character of treating agent
1	Gas	Gas
2	Gas	Liquid
3	Gas	Solid
4	Liquid	Gas
5	Liquid	Liquid
6	Liquid	Solid
7	Solid	Gas
8	Solid	Liquid
9	Solid	Solid

1. Treatment of Gas by Gas.—Since the phenomena under consideration involve treatment of a mixture by an agent immiscible with one of its components and since, in the absence of chemical combination or unusual affinity, all gases are miscible in all proportions, it follows that this particular case is never encountered.

2. Treatment of Gases by Liquid (Gas Washing or Scrubbing).—One of the best methods of separating the components of mixtures of gases or vapors is by means of selective absorption in

liquid solvents. Thus, while the solubility of coal gas in water is very small, the solubility of ammonia in water is great. Consequently, if one treat coal gas with a relatively small amount of water, it is possible to remove from it by solution in the latter practically all of the ammonia originally in the gas. Furthermore, the ammonia can then be readily separated from the water by distillation. Similarly, vapors of benzene, toluene and xylene in coal gas can be dissolved in various absorbent oils, gasoline can be removed from natural gas by these same solvents, sulphur dioxide can be recovered from smelter gases by water, carbon dioxide from flue gases by aqueous solutions of alkali carbonates, water vapor from air by sulphuric acid, and the like. In the last illustration the purpose is to free the air from water rather than to recover the water, whereas in most cases it is essential to recover the component dissolved. This difference in purpose, however, in no wise affects the character of the absorbing operation itself, although in general it will influence the method of treatment of the absorbent before re-use.

3. Treatment of Gases by Solids.—It has long been known that many solids show selective adsorption for specific gases and vapors. Thus, the adsorptive capacity of palladium for hydrogen is so high that this metal may be employed for the quantitative absorption of hydrogen from mixtures with other gases. Similarly, the adsorptive capacity of special charcoals for gases has long been known. During the war charcoal and other solid adsorbents were employed in gas masks for the removal of the poison gases employed in chemical warfare. Thus, a fraction of a liter of activated charcoal in a gas mask canister was found capable of reducing the mustard-gas concentration of air, inhaled at a rate as high as 60 liters per minute, to below one part in 100,000,000. Largely as a result of improvements during the war in the manufacture of activated charcoal, silica gel, and other highly active adsorbents, the use of these materials for adsorption of gases is being widely introduced in industrial plants. A number of plants for the recovery of gasoline from natural gas by charcoal are already in operation in this country.

4. Treatment of Liquid by Gas or Vapor (Steam Distillation and Stripping).—The benzene dissolved in absorbent oil in the recovery of light oil from coal gas, referred to under Par. 2, is removed from the relatively non-volatile absorbent by heating,

to increase the volatility of the benzene, and by blowing through steam to sweep out the benzene vapor. This operation is ordinarily described as oil stripping or denuding. In principle it is absolutely analogous to the steam distillation of a volatile component from a non-volatile liquid already treated on pages 565 to 569, and on pages 595 to 598.

5. Treatment of Liquid by Liquid.—It is sometimes advantageous to remove organic compounds from aqueous solutions by extraction with suitable organic solvents, such as ether, benzene, naphtha, and the like, in which they are more soluble than in water. This makes it possible to separate them from other substances which may accompany them in the water solution but which are not soluble in the solvents employed. Thus, the standard method for the analytical determination of unsaponifiable oils and waxes in admixture with fatty material is to submit the mixture to vigorous saponification with alcoholic potash or, if necessary, sodium ethylate, and to dilute the product with water and extract with petroleum ether. The soaps remain in the aqueous solution while the unsaponifiable oils and waxes dissolve in the ether.[1] It is sometimes advantageous to modify the relative solubilities by adding a material soluble in one liquid but not the other; thus the addition of salt to an aqueous solution prior to extraction with ether improves the separation.

Liquid SO_2 is employed to separate aromatic and highly unsaturated hydrocarbons from solution in liquid paraffins and naphthenes (Edeleanu process), taking advantage of the much greater solubility of the aromatics and unsaturateds in SO_2. Processes of this sort have not in the past been employed on an industrial scale to the extent which their promise seems to justify. It is likely that, as the manipulative technique required is developed, their utilization will become far more frequent.

6. Treatment of Liquids by Solids (Percolation or Adsorption Filtration).—Liquids contaminated with organic coloring matters of complex structure and high molecular weight can often be

[1] Since the soaps are not entirely insoluble in the ether nor the unsaponifiable material in the aqueous solution, it is necessary to extract the aqueous layer repeatedly with ether and to wash the ether solutions with water, these washings being added to the main aqueous solution. The unsaponifiable material is recovered by evaporation of the ether from the combined ethereal extracts.

freed best from these impurities by treatment with suitable solid adsorbents such as bone char, activated charcoal, fuller's earth, and the like. Such treatment is used for the decolorization of sugar syrups, animal, vegetable and mineral oils, etc. It is often advantageous to allow the liquor to percolate through the relatively coarse, granulated solid. The color is usually taken up by the solids by the mechanism of adsorption (see pp. 643–649).

7. Treatment of Solids by Gases.—When gasoline or similar materials have been adsorbed on charcoal, as described under Treatment of Gases by Solids, the gasoline must be removed from the charcoal so as to recover it and make it possible to employ the adsorbent over again. This may be accomplished by sweeping over the charcoal a current of superheated steam which picks up the gasoline and carries it out to a condenser where both gasoline and steam are liquified and separated by decantation.

8. Treatment of Solids by Liquids (Lixiviation, Leaching, and Extraction).—Black ash consists essentially of a mixture of sodium carbonate and other water-soluble compounds, with insoluble constituents; caliche, of sodium nitrate mixed with insolubles; tanbark, of soluble tannic acid adsorbed on the fibers of the bark. All these materials can be recovered by solution in water, though the processes differ because in the first cases the materials dissolved are very soluble, while in the last they are quite firmly held by the insoluble residue. Also, wool grease is removed from wool and vegetable oils from press cake, by solution in naphtha or other suitable organic solvents, etc. These processes are called extraction, but in principle do not differ from those already enumerated (see pp. 715 and 721).

9. Treatment of Solids by Solids.—The transference of a material from one solid to another is so slow and the separation of mixed solids so difficult that this case does not arise in practice.

PART II. FACTORS CONTROLLING OPERATION

Equilibrium.—Whenever a substance distributes itself between two materials, a distribution equilibrium always tends to be set up. Thus, if SO_2 gas, whether or not mixed with inert gas, be brought into contact with water at 20° C., the SO_2 will continue to dissolve in the water until its concentration in the water is sixty times that in the gaseous phase. This condition represents equilibrium, and no further solution of the gas will occur unless this equilibrium be disturbed. If water containing dissolved SO_2 be brought in contact with gas containing less than one-sixtieth as much SO_2 per unit volume as the water, SO_2 will escape from the water and pass into the gas until the ratio of the concentrations in the two phases has reached the equilibrium value given above.

If one wish to remove SO_2 from a gaseous mixture by water, it is obvious that this equilibrium sets an absolute lower limit on the amount of water necessary to employ for complete removal. Equilibrium is therefore a vital factor in controlling the operation of absorption systems. In the case cited above, the equilibrium is extremely simple in character, but frequently the relationships are complicated. Specific cases of importance will be discussed on pages 637 to 643.

Rate of Reaction.—The transference of a substance from one body to another obviously requires time. Other things equal, the rate of transfer will be proportional to the surface of contact between the phases and consequently, to secure rapid interaction, the interfacial surface should be made as large as possible. Furthermore, transference in general requires diffusion through the surface films at the interface (see Chap. XIX). This diffusion will be proportional to the concentration gradient, and consequently the rate of transfer will be greater the greater the distance from equilibrium. Factors, such as agitation, which decrease the thickness of surface films will tend to increase diffusion rate and, similarly, factors which increase specific rate of diffusion, such as rise in temperature of a liquid, will also be helpful, though the latter will frequently throw equilibrium the wrong way to an extent more than compensating for increased diffusion rate. Reaction rate is no less important an influence in operation than equilibrium itself.

Counter-current Action.—Since the transfer of a substance from one material to another cannot possibly go beyond equilibrium and since, in general, low concentration of the substance in one material corresponds at equilibrium to low concentration in the other, it follows that a single treatment of the original material cannot remove any large fraction of the substance to be transferred unless one employ a relatively large amount of treating agent or the treating agent have a great affinity for the

substance absorbed. The disadvantages of employing excessive amounts of treating material are obvious, and where the affinity of the treating material for the substance absorbed is great, the difficulty of removing it later is also serious. One can, therefore, lay down the rule that a single treatment is usually impractical and unsatisfactory. However, if one will treat the original material with treating agent which has been previously employed and which, therefore, is already partially saturated with the substance to be transferred, it becomes possible, due to the high concentration in the original material to be treated, to raise the saturation of the treating agent to a point at least approaching equilibrium. At the same time it becomes practicable finally to reduce to a very low point the concentration in the original material by treating it ultimately, after a number of intermediate steps, with fresh treating agent in which the concentration of the substance to be recovered is negligible. This systematic, stepwise interaction of two materials is described as counter-current treatment (see pp. 637 to 677). Counter-current action is capable of varied applications (see pp. 173 and 231), but for diffusional processes its use in some form is almost always essential.

Temperature Control.—There is frequently a marked temperature effect accompanying the transfer of material from one phase to another. Thus, in the absorption of a vapor from a gas by a liquid, the latent heat of condensation of the vapor is set free, and this heat raises the temperature of both the liquid and the gas. Since, in general, rise in temperature decreases the solubility of the gas or vapor in the liquid, the equilibrium and therefore also the absorption rate are both adversely affected. Where the concentrations of the substance transferred are small, the heat capacity of the other materials present is usually so great that the temperature rise is not serious, but where concentrations are high, this factor may be very important. It must never be forgotten and, where necessary, means must be provided to control the temperature.

Recovery of Treating Agent.—Occasionally the treating agent is either air or water and the material absorbed thereby is to be discarded, but ordinarily the treating agent must be freed from the material which it has taken up and used over again. It is therefore essential to choose the treating agent not only from the

point of view of its effectiveness for the original absorption but also from the standpoint of ease of separation and recovery. Furthermore, in order to make the original treatment as complete as possible, it is necessary to remove the absorbed material from the treating agent very completely before re-use. It is obvious that the larger the amount of treating agent employed, the greater the expense of purifying it. Consequently, from this point of view, it is desirable to keep the amount of treating agent low and the concentration of absorbed material in it high, a result attainable only by effective counter-current action. Reduction of the amount of treating agent, while it reduces the cost of its purification, tends to decrease the completeness of recovery from the material treated and, by reducing the rate of absorption, to increase the cost of treating. There is, therefore, an economically optimum ratio of treating agent to material treated, the value of which will depend on the cost factors governing each individual case.

PART III. EQUILIBRIA

Introduction.—If, in any *single* phase of matter, there exist at different points differences of concentration of any compound in it, that component tends to diffuse from a point of high to a point of low concentration. With diffusion through gases and liquids all are familiar, but diffusion also takes place through solids. Thus gold diffuses through solid lead and hydrogen through palladium. The diffusion of carbon through iron at temperatures hundreds of degrees below the melting point is exploited in both malleabilization and case hardening. The last is diffusion through a multiphase solid, but the first two are probably single phase. Fick's law states that the rate of diffusion is proportional to the concentration gradient at the point in question and is of course proportional to the area of cross-section through which diffusion is taking place. Diffusion is therefore analogous to conduction of heat (see pp. 118–187 and 441–480).

On the other hand, at the *interface* between phases, diffusion or net transfer of material from one phase to the other, does not of necessity result from a concentration difference between the phases but depends on the *equilibrium* relationships between them. Thus, while the concentration of water molecules in liquid water is far higher than in steam, the two phases can still

be in equilibrium or, if the steam be at a somewhat higher pressure it will condense into the water; *i.e.*, water molecules will pass from a point of low concentration (the steam) to one far higher (the liquid water). Similarly, if air at 0° C. contain hydrochloric acid gas in a concentration of only 0.001 mm. per cubic centimeter and this air be brought into contact with water, the HCl will continue to dissolve in the water phase until it has built up a

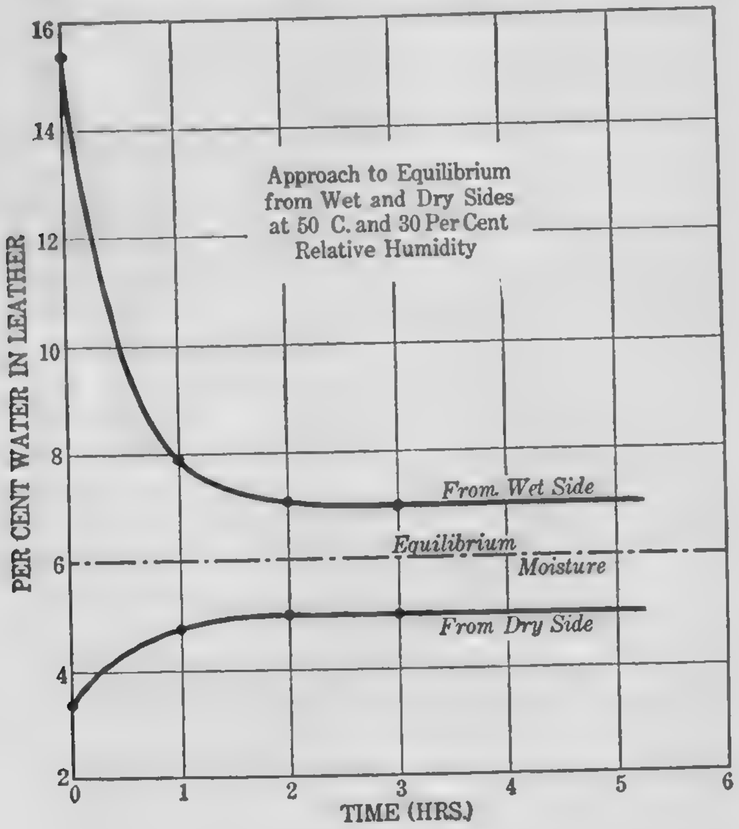


FIG. 162.

concentration of over 15 per cent, *i.e.*, 170 mg. per cubic centimeter, a concentration 170,000 fold that in the air from which the acid came. Only in case the HCl concentration in the water be greater than this will HCl pass from the water into the gas. There is, therefore, in general, even at equilibrium, a sudden concentration break at the interface. It is obvious that these equilibria between phases are of controlling significance in processes of absorption, extraction, and the like.

The technique of the determination of interphase equilibria is exceedingly important and data should never be accepted without reservation unless obtained by one skilled in the art. One of the essential things is to approach equilibrium from both sides, to make sure that one is not dealing with false equilibria or other complicating phenomena. Furthermore, this frequently saves time, because one can quickly enough come to so short a distance from the true equilibrium on the opposite sides, that taking the mean of the two approximate values thus obtained gives the desired result with a precision in many cases sufficient. Figure 162 shows the approach to equilibrium from both sides[1] for the drying of oak-tanned sole leather, ground to reduce the time required in reaching substantially constant weight.

In discussing the various important types of equilibria, the following classification has been adopted.

1. Linear distribution:
   - *a.* Gases and Liquids.
   - *b.* Liquids and Liquids.
   - *c.* Special cases.
2. Adsorption:
   - *a.* Solids and Gases.
   - *b.* Solids and Liquids.
   - *c.* Gases and Liquids.
3. Complete chemical combination.
4. Incomplete chemical combination.

1. Linear Distribution

Gases and Liquids.—There are certain important cases in which at equilibrium, the concentration of the common component in one phase is proportional to that in the other. The most familiar case is that of the solubility of gases which follow Henry's Law, *i.e.*, in which the concentration of the gas dissolved in the liquid is proportional to the partial pressure of that gas in the gaseous phase above the liquid. Since the concentration of a gas in a mixture of gases is proportional to its partial pressure, the above is equivalent to saying that the concentration of gas dissolved in the liquid is proportional to the concentration of that gas in the gaseous phase in equilibrium with the liquid (see p. 584).

[1] A. C. PHELPS, Undergraduate Thesis, Chemical Engineering, M. I. T., 1921.

Figure 163 shows the solubility[1] of a number of important gases as a function of the temperature. It will be noted that rise in temperature decreases the solubility. It is important to remember that the solubility is proportional to the partial

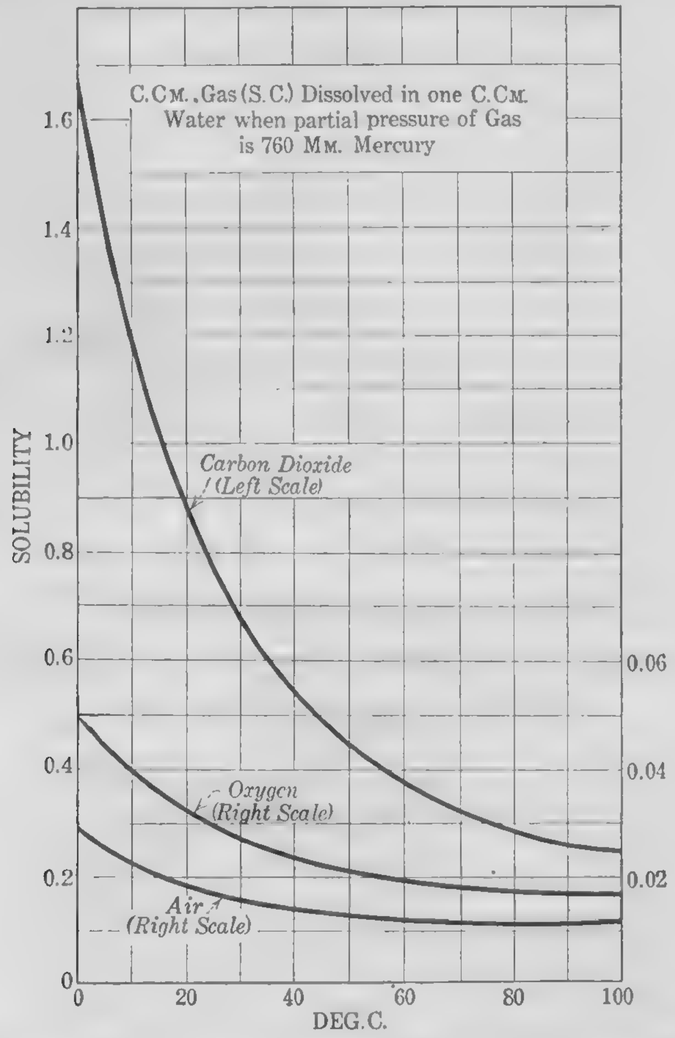


FIG. 163.—Effect of Temperature on Solubility of Gases in Water.

pressure of the gas and not to the total pressure above the liquid. Thus, the solubility of oxygen in water at 100° C. is 0.017 volume per unit volume of water, provided the partial pressure of the

[1] BOHR and BOCK, *Wied. Ann.*, **44** (1891), 318.

oxygen be 1 atmosphere. If, however, the total pressure be 1 atmosphere at this temperature, this must consist entirely of water vapor[1] and the solubility of oxygen in the water under these conditions is zero. To dissolve the amount of oxygen quoted above at this temperature, the total pressure must be 2 atmospheres, the partial pressure of the water and of the oxygen each being 1 atmosphere. In other words, the solubility of gases in liquids at the boiling points of the latter are zero, a fact made use of in the deaeration of liquids. Modification of the form in which the concentration in the liquid is expressed will sometimes broaden the range over which Henry's law holds; acetylene dissolved in acetone is a case in point.

Since Raoult's law (see p. 582) may be written in the form $p = Px$, it is obvious that it may be looked upon as a special case of linear distribution between the gaseous and liquid phase.

Illustration 1.—Flue gases, containing 1 per cent benzene vapor by volume, are to be washed with a mineral oil containing 0.5 per cent benzene by weight. Calculate the maximum percentage of the original benzene that could be absorbed

(*a*) if the absorption were carried out at 20° C., and
(*b*) at 30° C.

Notes.—The vapor pressures of pure benzene (Fig. 7, p. 17) are 75 mm. of mercury at 20° C. and 120 mm. of mercury at 30° C. The molecular weight of benzene is 78.0. Over the range of concentrations and temperatures involved, Raoult's law may be applied to the partial pressure of the benzene by taking the average molecular weight of this mineral oil as 230. Assume that the barometer is 760 mm. of mercury.

Solution.—Since it is desired to reduce the benzene concentration of the flue gas to the minimum value, the exhausted gas must be in contact with the leanest oil. In other words, one must employ the counter-current principle (p. 635). To obtain the maximum recovery, the absorber must be infinitely tall, so that the benzene concentration in the spent gases will be in equilibrium with the leanest oil at the top of the tower. Under these conditions, at 20° C., the partial pressure of benzene in the exit gases will equal

$$75 \frac{\frac{0.5}{78}}{\frac{0.5}{78} + \frac{99.5}{230}} = 1.10 \text{ mm. of mercury}$$

Hence, at 20° C., the best that one can do will be to reduce the benzene from a pressure of 7.6 to 1.10 mm. To calculate the percentage of the original benzene, absorbed by the oil, take a basis or 1 mol of inert or benzene-free gas.

[1] Since the depressing effect of the dissolved oxygen on the vapor pressure of the water is negligible.

$$\text{Then } 100\frac{\frac{7.6}{760-7.6}-\frac{1.10}{760-1.10}}{\frac{7.6}{760-7.6}}=85.6 \text{ per cent recovery.}$$

Similarly, at 30° C., the maximum percentage recoverable is found to be 77.2, emphasizing the importance of low temperature as regards maximum per cent recovery (see, however, page 659).

Figure 164 shows the effect, on the per cent recovery, of changing the benzene concentration of the treating agent.

Liquids and Liquids.—Similarly, the distribution of a solute between two immiscible liquids is frequently linear; *i.e.*, at

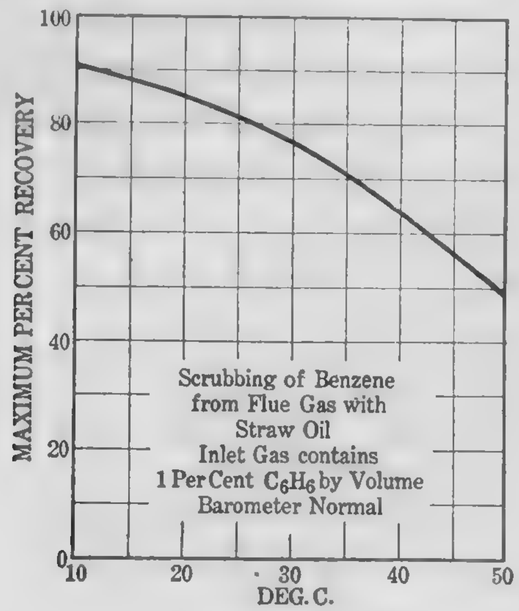


FIG. 164.

equilibrium the concentration of the solute in liquid A is proportional to its concentration in liquid B.

These two simple distribution laws are usually but not always valid at low concentrations. Thus, Henry's law almost always applies for sparingly soluble gases, because in such case it is obvious that the concentration of gas in the liquid phase cannot possibly be high. It likewise frequently applies to very soluble gases so long as the concentration in the liquid phase is low or, what is equivalent to the same thing, the partial pressure in the gaseous phase is very low. Similarly, the distribution of a

solute between two liquids of limited miscibility is usually linear so long as the concentration in the two phases is small. Whenever the concentration in a liquid phase becomes high, deviations from proportionality almost always begin to develop.

Special Cases.—Many solids are porous and, when impregnated with solutions, hold these solutions within their voids. In order to remove the solute from such a solid, it may be necessary to allow the solute to diffuse from the voids within the solid out into a less concentrated, external surrounding solution, thus to be washed away. The amount of solute held by such solids is obviously proportional to the concentration of the solution in the internal voids. Since such an internal solution will obviously be in equilibrium with an external solution, outside the solid, of equal concentration, it follows that the concentration of solute within the solid, expressed as a relation between the amounts of solute and solid is proportional to that of the external solution with which it is in equilibrium. Such cases are illustrated by leather, wood pulp, fabrics, etc., saturated with solutions of non-adsorbed materials.

One can have within the internal voids solutes present as solids in excess of that in solution within those voids. In such cases the mass will be in equilibrium with a saturated external solution of the solute at all concentrations of the solute within the solid, above that corresponding to a saturated solution just sufficient to fill the internal voids.

2. Adsorption

Solids and Gases.—Certain solids and gases combine to form compounds that may be loose or very stable, but which differ from compounds such as calcium carbonate, formed by interaction of calcium oxide and CO_2, in that first, the combination does not take place in constant stoichiometric proportions and second, the decomposition pressure is not independent of the amount of gas combined with the solid provided excess solid be present, but varies progressively with the gas quantity held by the solid. The data of a characteristic adsorption reaction, namely, that of CO_2 gas[1] on activated charcoal, are shown in Fig. 165.

It will be noted that, at very low partial pressures of the CO_2, relatively large quantities of the gas are held on the solid. As the partial pressure of the gas is increased, the amount held on the solid at equilibrium also increases, but at a much less rapid rate than would correspond to linear distribution. Finally a point is reached at which a relatively large increase in partial pressure

[1] LOWRY and HULETT, *Jour. Am. Chem. Soc.*, **42** (1920), 1393.

of the gas is required to force a given increase of gas on the solid. Figure 165 shows also the data for the adsorption of benzene vapor on charcoal.[1]

A similar curve for a more loosely held gas, nitrogen,[2] is also shown in Fig. 165. While the general shape of the curve

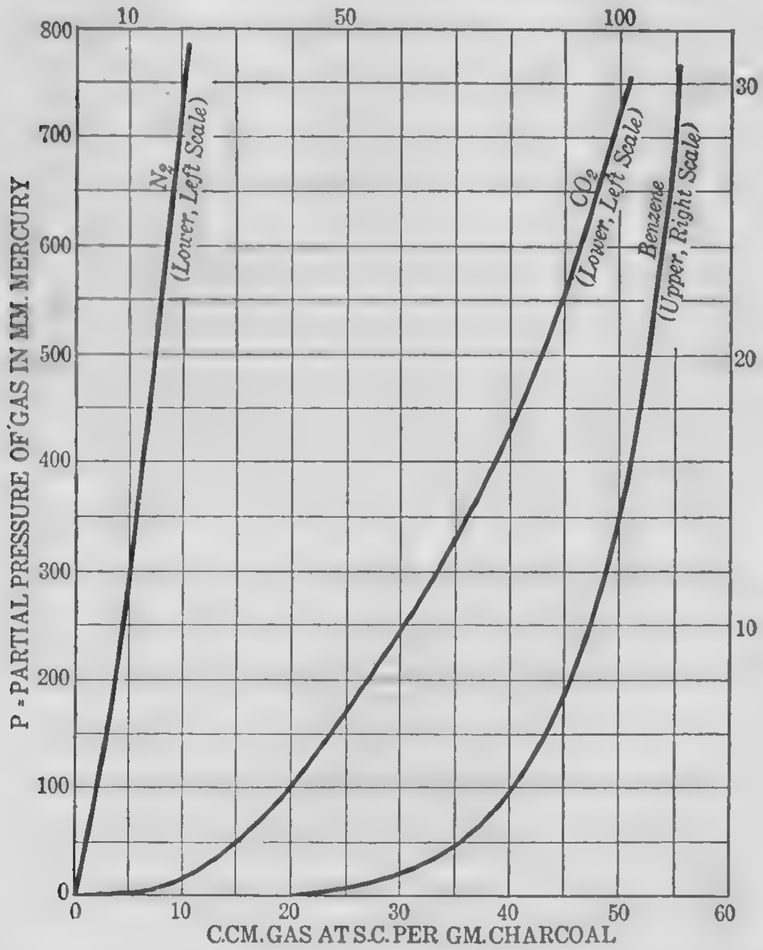


FIG. 165.—Adsorption Equilibria for Gases on Charcoal (Rectangular Co-ordinates).

is the same, the difference lies in the fact that much less gas is held by the solid at low partial pressure of the gas.

Mechanism.—The exact mechanism of adsorption is still a matter of dispute. It seems certain that in some cases adsorption is due to chemical combination of the gas with the free valences of atoms on the surface of the solid. In other cases the evidence indicates that adsorption is due to liquefaction of the gas and its retention by capillary action in the exceedingly fine pores of the adsorbing solid. In some cases the two phenomena are probably superimposed. Often one encounters curves of the type shown in Fig. 109 (p. 489) for water adsorbed on cotton, in which at low pressures one gets a characteristic adsorption relationship, the water held flattening out to an approximately asymptotic value, followed later by a further rise in adsorption at high partial pressures of the adsorbed gas. It has been surmised that the first part of the diagram may represent chemical adsorption and the latter, capillary effects; or it may be that the first part represents liquid held in exceedingly fine capillaries and the latter, the influence of capillaries an order of magnitude larger in size.

[1] BERL and ANDREWS, *Zeit. fur angew. Chem.*, **34** (1921), 381.

[2] LOWRY and HULETT, *loc. cit.*

Freundlich Equation.—Whatever the mechanism, the equilibrium between a gas or vapor and an adsorbing solid is generally exponential in character over certain ranges in concentration. This relation is expressed by the Freundlich equation,

$$x = ap^{1/n}$$

where x is the amount of the gas adsorbed per unit quantity of adsorbing solid, and p is the partial pressure of the gas in equilibrium with the solid; a and n are constants. x and p may be expressed in any convenient units. The numerical values of a depend on these units and of both a and n on the specific nature of both gas and adsorbent. In true adsorption, n is always greater than unity.[1] The more firmly the gas is adsorbed, the greater is the numerical value of n. The quantity a is proportional to the active surface of the adsorbing solid. While it has been claimed that this equation has theoretical basis, it is probably safer to regard it as empirical in character. The data demonstrate that it is not exact, but as an interpolation formula over very wide ranges it is extremely valuable. Numerical illustrations of this equation will be found in pages 718 and 720. From

[1] If $n = 1$, one is dealing with a phenomenon of solution which follows Henry's law and which is not classified as adsorption. The solubility of CO_2 in solid rubber is a case in point. See VENABLE and FUWA, *J. Ind. Eng. Chem.*, **14** (1922), page 139. If n is less than unity, the phenomenon is sometimes called negative adsorption, but is of minor technical importance.

the form of the equation it is obvious that if one plot, on logarithmic paper the partial pressures of the gas as ordinates against the equilibrium concentrations on the adsorbing solid as abscissae, the equation demands that the data fall on a straight line, the slope of which is equal to the exponent $1/n$ (see Fig. 166). This offers a ready means of testing the applicability of the Freundlich equation to any given set of data.

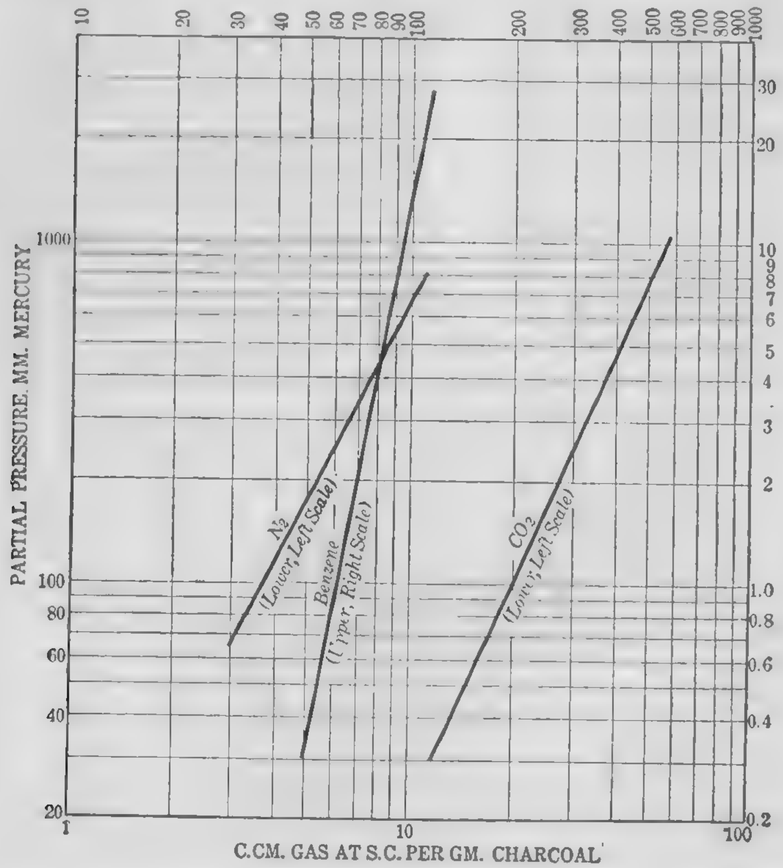

PARTIAL PRESSURE MM. MERCURY
C.CM. GAS AT S.C. PER GM. CHARCOAL
N2 (Lower, Left Scale)
Benzene (Upper, Right Scale)
CO2 (Lower, Left Scale)

FIG. 166.—Adsorption Equilibria for Gases on Charcoal (Logarithmic Co-ordinates).

While adsorptive phenomena are to no small degree specific in character, it is none the less possible to lay down the general rule that the higher the molecular weight and the lower the volatility of any gas, the greater its tendency to adsorb on any solid. So marked is the influence of volatility, *i.e.*, the vapor pressure of the liquefied gas in the pure state, that it is often

better to express the concentration of the adsorbed gas, not as its partial pressure in the gaseous phase, but as the ratio of its partial pressure to that of its saturation pressure.[1] Expressed in this way it is found that the influence of temperature on the equilibrium is relatively slight.[2] The adsorption equilibria of water on textile fibers at various temperatures are plotted in Fig. 109 (p. 489). As vapor saturation is approached, the Freundlich equation always breaks down.

Selective Adsorption.—So important is the effect of volatility that it is frequently possible for a gas of low volatility to displace one of high. Thus, if activated charcoal be brought in contact with natural gas, it adsorbs a certain amount of all the hydrocarbons of the gas. On the other hand, per unit partial pressure the high boiling constituents of the gas are adsorbed selectively, that is, far more completely than the low boiling. Furthermore, if this same charcoal be treated with additional gas, the high boiling components of this second quantity of gas will adsorb on the charcoal and in order to do so will to a large degree displace the low boiling constituents already adsorbed. In this way a charcoal which has picked up from a gas relatively large quantities of methane, ethane, and propane will, when treated with further gas, adsorb pentane, hexane, and higher hydrocarbons by displacing the lower boiling ones already picked up. This is the reason for the fact that by the intelligent use of activated charcoal in recovering gasoline from natural gas it is possible to produce a product relatively free from gases of low molecular weight.

Importance of Surface.—The concentration of adsorbed gas or vapor per unit area of adsorbing solid is exceedingly low, *i.e.*,

[1] In the case of water this ratio is of course the ordinary relative humidity (see p. 441). The term *relative humidity* is not infrequently applied to the concentration of vapors other than water when expressed in the same way.

[2] In certain cases, as in the adsorption of SO_2 by silica gel, equilibrium data at various temperatures may be correlated by the Freundlich equation modified as follows:

$$x = a(rs)^{1/n},$$

where r is the relative humidity as previously defined, and s is the surface tension. Expressing x as cubic centimeters of liquid SO_2 per grams of gel, McGAVACK and PATRICK, *J. Am. Chem. Soc.*, **42** (1920), 916, found n to be 2.24 between −80° C. and +100° C.

the adsorbed film is very, very thin. Therefore, in order to adsorb large quantities of gas it is essential to have an enormous amount of adsorbing surface. This might be secured by having the adsorbing agent finely subdivided. Because of the difficulties of handling powders, however, it is preferable that the adsorbing agent consist of a spongy, porous material, agglomerated into granules so that each individual lump is relatively large but, because of its porous structure, the total surface is enormously greater than could be realized with a dense solid of

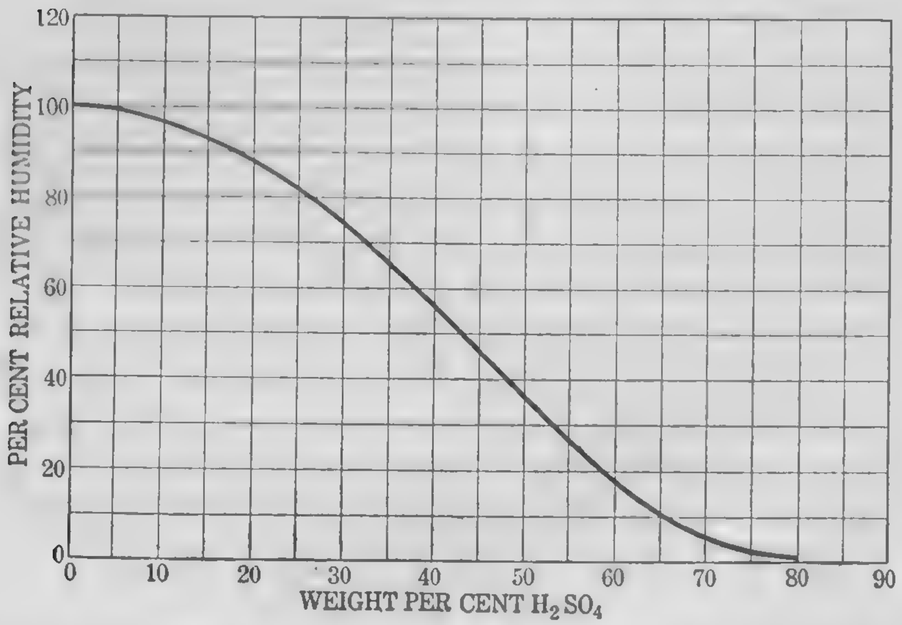


FIG. 167.—Equilibrium Distribution of Water between Air and H_2SO_4. (See also Fig. 172, page 678.)

the same grain size. Thus the apparent density of the individual granules (best called grain density) of well-activated charcoal is about 0.83,[1] while that of the carbon itself is 1.89. Thus the granule itself contains 56 per cent capillary voids.

Solids and Liquids.—Solids can adsorb solutes from solution in liquids by a mechanism entirely analogous to the adsorption of gases. Here also the Freundlich equation applies. Cases in point are the adsorption of direct dyestuffs by textile fibers, the adsorption of tannic acids by both hide substance and vege-

[1] This must not be confused with apparent density, *i.e.*, the weight, per unit volume of the granules in bulk, which in this case is 0.46.

table fibers, the adsorption of organic colors by fuller's earth, bone char, activated charcoal, and the like. Computation methods do not differ in principle from those employed for the adsorption of gases by solids.

Gases and Liquids.—While gases and vapors adsorb on the surface of liquids, it is but rarely that liquids can be employed in a permanent state of subdivision sufficiently great to furnish the surface necessary to adsorb appreciable quantities. On the other hand, liquids dissolving gases sometimes give equilibrium diagrams extremely similar to adsorption curves. These are usually liquids which chemically combine with the dissolved material. A case in point is that of sulphuric acid and water, the equilibrium diagram for which is given in Fig. 167.[1] In such cases computations may be made by the same methods employed for solid adsorbents. (See p. 645 and pp. 675 to 679.)

3. Chemical Combination

When a gas is treated with an absorbent with which it combines chemically to form a stable compound, so long as there is excess of this absorbing agent, at equilibrium the partial pressure in the gaseous phase is negligible. Thus, if one is absorbing ammonia in excess sulphuric acid, as in the manufacture of ammonium sulphate from illuminating gas, or CO_2 in excess caustic, as in gas analysis, or the like, the gas left undissolved after thorough contact between the gaseous and liquid phases is attained is negligible. Similarly, if one is absorbing a gas by a solid, with which it firmly combines chemically, such as CO_2 by calcium oxide in the purification of air for liquefaction, the absorption is complete so long as contact is adequate and the absorbent is present in excess.

4. Incomplete Chemical Combination

In many cases the combination is a loose and unstable one; however, *i.e.*, the compound is subject to partial dissociation. Such cases are obviously governed by the law of mass action. Thus, when carbon dioxide for liquefaction is recovered from flue gas, it is dissolved in a solution of alkali carbonate, the carbon dioxide combining to form bicarbonate, the solutions of which

[1] R. E. Wilson, *Jour. Ind. Eng. Chem.*, **13** (1921), 326.

exert a very decided partial pressure of CO_2, due to dissociation. The relationship[1] is given by the mass action expression[2]

$$p_{co_2} = \frac{f^2 N}{kK(1-f)},$$

where f = the fraction of total base present as bicarbonate.
N = normality of solution with respect to the base.
K = mass action "constant" which varies with concentration and temperature.
k = solubility coefficient of carbon dioxide in water, which varies with temperature as shown on Fig. 163 (p. 640).

Other cases undoubtedly involving loose chemical combination are of a character such that it is difficult to demonstrate this quantitatively. A case in point is the absorption of water vapor by sulphuric acid, the equilibrium data for which are found in Fig. 167.

An interesting case of chemical combination is found in the distribution of certain substances between liquids in which the substance in question exists in different degrees of polymerization. Thus, acetic acid dissolves in benzene in the form of double molecules and in ether as single molecules. If one grant the presence in the benzene solution of a small proportion of single molecules, the concentration of which is in equilibrium both with the double molecules in that solvent and the single molecules in the ether, the law of mass action requires that at equilibrium the distribution of the acetic acid between the two solvents be determined by the following equation:

$$y^2 = kx,$$

where y = the concentration of acetic acid in ether.
x = the concentration of acetic acid in benzene.
k = the distribution constant.

When a gas combines chemically with a solid to form a second solid phase present as such, the compound must dissociate, giving a constant partial pressure of the gas so long as any of the compound and both its dissociation products are present. Thus, if calcium oxide absorb CO_2 to form calcium carbonate, so long as all three of these substances are present, equilibrium can exist only at a certain partial pressure of CO_2, the value of which depends on the temperature and on nothing else. Because of this fact it can be laid down as a general rule that chemically combining solid absorbents are unsatisfactory; for, if the compound formed is one readily dissociating, its partial pressure is relatively high and, since combination cannot take place if the partial pressure of the gaseous component is below the equilibrium pressure, it is impossible to get complete absorption; on the other hand, if the compound be a stable one and the equilibrium pressure correspondingly low so that absorption can be complete, the very stability of the compound formed makes it difficult to decompose it and therefore hard to recover the absorbent for re-use. Thus, while it is true that calcium oxide is an excellent absorbent for CO_2, to recover the calcium oxide for re-use, the carbonate must be heated to approximately 900° C.

[1] In the derivation of this expression, the activities of the ionic constituents are assumed proportional to their total concentrations. See LEWIS and RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., 1923.

[2] H. N. McCOY, *J. Am. Chem. Soc.*, **29** (1903), 437; BYRNE and CARLSON, M. S. Thesis in Chem. Eng., M. I. T., 1921. See also WALKER, BRAY, and JOHNSTON, *J. Am. Chem. Soc.*, **49** (May, 1927), 1235.

PART IV. RATE OF ABSORPTION AND EXTRACTION

Introduction.—All available data indicate that phases in contact are, at the interface itself, always at equilibrium, or substantially so. For the interaction between liquids and gases, the data are quite conclusive; in interaction of solids and liquids, equilibrium at the interface has been demonstrated to exist when crystals dissolve in suitable solvents; in the case of solid absorbents, whether reacting with gases or liquids, the phenomena are complicated and the available data of accuracy sufficient to serve as a basis for a conclusion decidedly limited, but none of the data are incompatible with the above generalization, and throughout this treatment equilibrium at the interface will be assumed.

This assumption of equilibrium at the interface is equivalent to the assumption of exceedingly rapid interaction between the phases at the exact point of contact. It does not assume that this interaction is infinite in rate but that it is so rapid that it is not a controlling factor in delaying the ultimate result. Hence, it follows that the thing which controls the rate of interaction of phases is diffusion through the surface films and that, therefore,

the capacity of every apparatus for absorption or extraction is limited by and dependent upon diffusional phenomena. Consequently, in processes of absorption and extraction, the quantitative diffusional relationships are just as important as the equilibrium itself.[1]

1. Gases and Liquids

In the main body of either liquid or gas, except under special conditions which will not be considered here, mixing by convection is so rapid that the concentration of solute in the fluid is essentially uniform at all points. Differences in gas or liquor concentration due to "channeling" in absorption apparatus are not involved in this concept. On the other hand, the surface films are practically free from convection currents and consequently any transfer of solute through these films must be effected by the relatively slow process of diffusion. These films, therefore, offer the controlling resistances to the transfer of a material from one phase to another.

Diffusion through the gas film proceeds at a rate that is proportional to the difference between solute concentrations in the gas on the outside and inside of the film.[2] Diffusion through the liquid film, on the other hand, is controlled by the difference between the concentration of the solute in the liquid at the interface and its concentration on the other side of the liquid film, *i.e.*, in the main body of the liquid. Since the surface films are generally thin, the actual amount of solute contained in them at any one time is usually negligible compared to the amount diffusing through them. It follows, therefore, that all of the solute which passes through one film must also pass through the other, and as shown by Whitman[3] the two films may be consid-

[1] When a material diffuses from one substance to a second substance existing as a separate phase, the principles are the same regardless of whether the materials diffused from a gas into a liquid, or from a liquid into a gas. This applies to the transfer of a vapor from gas to solid, and from solid to gas. To cover such diffusion in either direction, the term *interaction* is here employed.

[2] Resistance to diffusion due to a gas film is, of course, non-existent in the special case where an absolutely pure gas is being absorbed. This problem is very rarely encountered in practice, however, since the presence of very small amounts of inert gas, which will concentrate at the liquid surface, is sufficient to create an effective gas film.

[3] The Two-film Theory of Gas Absorption, *Chem. Met. Eng.*, **29** (July 23, 1923), 147.

ered as two diffusional resistances in series. Under certain circumstances the importance of one of the films may be so much greater than that of the other that the second film may be neglected and the problem treated as if only one film existed (see p. 655).

The concentration difference through either of these films represents the potential or driving force that is causing diffusion to take place. If the concentration differences be expressed in identical units, *e.g.*, gram mols per liter, it is readily seen that the specific conductivity of the gas film will be much greater than that of the liquid. The only resistance encountered by the diffusing molecules is due to their collisions with the interfering molecules of the gas or liquid through which diffusion is taking place. Because of the greater density of the liquid the collisions in the liquid are much more frequent and the diffusional resistance is correspondingly greater than in the gas. The resistances to absorption, however, are dependent also upon the film thicknesses. It is to be expected that the gas film would be somewhat thicker than the liquid, because under comparable conditions of disturbance the major factor in determining film thickness is probably the ratio of viscosity to density and this ratio[1] is greater for gases than for liquids. Despite this fact, the greater specific conductivity of the gas film far more than overbalances the greater film thickness, so that the actual diffusional resistance encountered in the liquid film is much greater than that in the gas.

The amount of solute transferred per unit time by diffusion through the two films is $dW/d\theta$. (See table of nomenclature on p. 661) for resume of all symbols.) The amount of diffusion is obviously proportional to the surface of the interface S, and it is therefore convenient to refer to the diffusional current density $dW/Sd\theta$. This quantity is equal to the diffusion coefficient (k_G for a gas film or k_L for a liquid film) multiplied by the concentration difference available as a driving force, *i.e.*,

$$\frac{dW}{Sd\theta} = k_G(P_G - P_i) = k_L(C_i - C_L) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P = gas concentration.

C = liquid concentration.

[1] As pointed out on p. 76, this ratio is sometimes called kinematic viscosity.

The subscripts G, i, and L refer respectively to conditions at the outside of the gas film, at the interface, and at the inside of the liquid film.

It is clear that the numerical value of the diffusion coefficients k_G and k_L will depend upon the units in which the gas and liquor concentrations are expressed. The choice of these units is purely arbitrary. In this chapter, unless otherwise specified, solute concentration in the gas is expressed as its partial pressure in atmospheres and concentration in the liquid as grams per cubic centimeter because of the convenience of these units. This makes the separate values of k_G and k_L of the same order of magnitude for many cases.

The data at present available indicate that at the true interface between liquid and gas the two phases are substantially at equilibrium (P_i in equilibrium with C_i), even though there may be rapid diffusion and therefore high concentration gradients through the films on the two sides of that interface. This fact puts one in a position to visualize clearly what takes place in an absorption process (Figs. 168 and 169). Conditions at the outside of the gas film and at the inside of the liquor film are approximately the same as those in the main bodies of gas and liquid, respectively. Conditions at the interface are determined by two factors; first, the equilibrium between gas and liquor concentrations; and second, the fact that all the solute diffusing through the gas film must also diffuse through the liquid film. Thus,

$$P_i = f(C_i) \quad \ldots\ldots\ldots\ldots \quad (2)$$

this function being the solubility equilibrium relationship; and from Eq. (1),

$$k_G(P_G - P_i) = k_L(C_i - C_L) \quad \ldots\ldots\ldots \quad (3)$$

If the values of k_G and of k_L are known, the values of P_i and C_i, the interfacial concentrations, are at once determined by these two considerations. If, for example, k_G should be just equal to k_L to satisfy Eq. (3), $(P_G - P_i)$ would have to equal $(C_i - C_L)$.

Effect of Solubility.—Certain simplifications of the general Eq. (1) are permissible when the conditions become such as to make one of the two films negligible in importance as compared with the other. Since these conditions are primarily determined

by the solubility of the solute, it is desirable to consider separately the very soluble gases, the slightly soluble gases, and those of intermediate solubility.

Case I. Very Soluble Gases.—The absorption of hydrogen chloride in water is typical for the very soluble gases. In dilute solutions this gas is so soluble that at 30° C. even a 20 per cent solution (0.18 g. per cubic centimeter) exerts a vapor pressure of hydrogen chloride of less than 0.2 mm. of mercury (0.00026 atmosphere). In this case the high solubility of the gas makes it possible to build up high concentration gradients through the liquid film, although the concentration in the gas at the interface may be very small.[1] In other words, once it reaches the interface, the hydrogen chloride is rapidly sucked into the liquid film, and the gaseous concentration P_i is maintained at a very low figure. The absorption rate for this extreme case will be determined almost solely by the rate of diffusion through the gas film under a difference in gaseous concentration substantially equal to P_g since the value of P_i is negligibly small in comparison with P_g. The general formula can therefore be simplified for very soluble gases to the form,

$$\frac{dW}{S d\theta} = k_G P_G \quad \ldots\ldots\ldots\ldots \quad (4)$$

and the problem treated purely as a case of gas-film diffusion.

The same result can be reached by a more mathematical treatment. Consider the absorption at 30° C. of hydrogen chloride by water from an air mixture in which the partial pressure of hydrogen chloride is 0.1 atmosphere. The gas at this pressure would be in equilibrium with a saturated solution containing 0.39 g. hydrogen chloride per cubic centimeter. The liquid concentration at the interface C_i would therefore be somewhere between the limits of zero (that of the main body of liquid) and 0.39 (that of a saturated solution). This concentration would be definitely fixed by Eqs. (2) and (3). For example, if the absorption conditions were such that $k_G = k_L$, the equations would be satisfied by $C_i = 0.1$ and $P_i = 0.000021$; if $k_G = 2k_L$, $C_i = 0.2$ and $P_i = 0.00037$; and if $k_G = 0.5\ k_L$, $C_i = 0.05$ and $P_i = 0.0000054$.

[1] This discussion neglects the tendency toward fog formation (see p. 42) when strong HCl gas is brought into contact with water, due to diffusion of water vapor from the liquid surface out into the gas, there to condense with the HCl gas.

It will be observed that in these three examples the value of P_i is so low compared to P_G that it can be neglected in the expression from Eq. (1),

$$\frac{dW}{Sd\theta}=k_G(P_G-P_i)$$

and one may substitute the simpler form of Eq. (4).

Figure 168 shows the film conditions diagrammatically, with the concentrations prevailing at the interface when $k_G=k_L$. The sudden rise in concentration at the interface is due to the solubility characteristics of this solute, *i.e.*, a low partial pressure in the gas in equilibrium with a high liquid concentration because the solute has a great affinity for the water phase. It will be noted that the concentration gradient through the gas film is essentially the same as it would be if no liquid film existed.

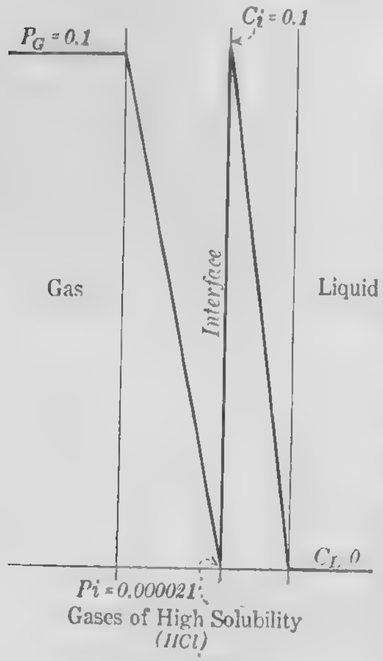


FIG. 168.

Case II. Slightly Soluble Gases. With gases of low solubility the rate of absorption is low because only very small concentration differences can be established across the liquid film. The solute diffuses so slowly through the liquid film that only a small concentration difference is required across the gas film. As a result the liquid at the interface is substantially saturated with solute at the pressure P_G, and it is unnecessary to consider the gas film in the calculations.

This may be shown mathematically for the absorption of oxygen at 0.1 atmosphere by oxygen-free water at 30° C. Saturation under these conditions corresponds to only 0.0000037 g. per cubic centimeter, and the value of C_i must therefore be between this saturation value and the zero concentration of the main liquid. As in the earlier example, C_i is determined by Eqs. (2) and (3). If $k_G=k_L$, $C_i=0.0000037$ and $P_i=0.0999963$; if $k_G=2k_L$, $C_i=0.0000037$ and $P_i=0.0999981$. It is evident that in all cases P_i is essentially the same as P_G; *i.e.*, the interfacial

conditions are practically the same as those existing in the main body of the gas. The value of C_i is therefore the same as that of a liquid saturated with oxygen at P_G, and may be expressed as C_G. It, therefore, becomes possible to express the rate equation as

$$\frac{dW}{Sd\theta}=k_L(C_G-C_L) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and eliminate any consideration of the gas film.

The film conditions for oxygen are represented in Fig. 169 with the concentrations prevailing when $k_G=k_L$. The sudden

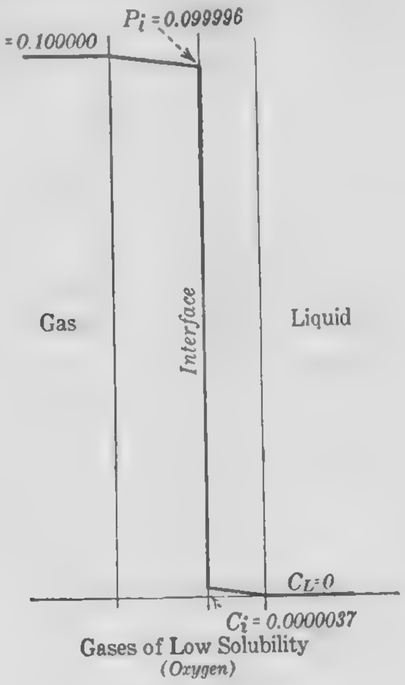


FIG. 169.

drop in concentration at the interface is due to the low solubility of this solute, *i.e.*, its slight affinity for the water phase. It should be noted that the relative slopes of the gas and liquid gradients are the same as in Fig. 168, since

$$\frac{P_G-P_i}{C_i-C_L}=\frac{k_L}{k_G}(=1 \text{ for both figures}).$$

In the diagram it is necessary to magnify the slopes of the gradients, since they would appear as horizontal lines if drawn to scale.

Case III. Gases of Intermediate Solubility.—There are many important cases where the gas is too soluble to permit one to neglect the gas film, Eq. (5), but is nevertheless not soluble enough to allow the liquid film to be disregarded, Eq. (4). General equation (1) must be used as the basis of calculation for such cases.

Henry's Law.—Fortunately, however, an overall coefficient, combining the two film coefficients, may be used whenever Henry's law holds over the concentration range in question. The concentration difference to be used with this overall coefficient is the total difference between gas and liquid, expressed in comparable units. Thus, if gaseous concentration is expressed as partial pressure P_G, the corresponding liquid concentration must be given as the equivalent partial pressure P_L in equilibrium with the liquid concentration C_L. Correspondingly, the gaseous concentrations must be expressed as C_G (the liquid in equilibrium with P_G) if the liquid concentration C_L is used.[1]

If the Henry's law relation is expressed as

$$C = HP \quad \ldots\ldots\ldots\ldots \quad (6)$$

the absorption equation becomes

$$\frac{dW}{S d\theta} = K_G(P_G - P_L) \quad \ldots\ldots\ldots \quad (7)$$

or

$$\frac{dW}{S d\theta} = K_L(C_G - C_L) \quad \ldots\ldots\ldots \quad (8)$$

and the *overall* coefficients K_G and K_L can be obtained from the *individual* film coefficients, k_G and k_L, by algebra, using Eq. (1), (6), and (7) or (8). Thus,

$$\frac{1}{K_G} = \frac{1}{Hk_L} + \frac{1}{k_G} = \frac{1}{Hk_L} \quad \ldots\ldots\ldots \quad (9)$$

and

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{H}{k_G} = \frac{H}{K_G} \quad \ldots\ldots\ldots \quad (10)$$

From the nature of the overall coefficients, it will be seen that the overall coefficient K_L can never be greater than the liquid-film coefficient K_L and, similarly, that K_G can never be greater than k_G.

[1] BOHR, *Am. Phys. Chem.*, **68** (1899), 500; LEWIS, *J. Ind. Eng. Chem.*, **8** (1916), 825; DONNAN and MASSON, *J. Soc. Chem. Ind.*, **39** (1920), 236.

It should be noted that theoretically the overall Eqs. (7) and (8) can be applied only to isothermal absorptions, since the coefficient of Henry's law changes with temperature. In practice, however, it is permissible to employ this method over narrow ranges of temperature.

Other Cases.—The methods of computation for soluble gases which do not approximately obey Henry's law over the range being studied, and yet are not soluble enough to be treated under Case I, are best made by the methods given on pages 689 to 690. The absorption of hydrogen chloride in solutions of concentrated hydrochloric acid (which exert an appreciable vapor pressure of HCl) represents this type of problem.

Other Variables.—The discussion has so far considered only the effect of solubility of the gas in determining absorption rate per unit area. The other important variables are the diffusion coefficients k_G and k_L, which can be varied considerably by the character of the absorption process. Any factors which tend to cut down the thickness of the surface films should increase the coefficients and correspondingly speed up the absorption rate.[1] Thus, agitation of the liquid increases diffusion through the liquid film, while higher gas velocities past the surface cause more rapid diffusion through the gas film, see pp. 705 to 715.

The effect of such factors will be decidedly dependent upon whether the process is controlled by gas-film or liquid-film diffusion. Thus, a change that decreased the thickness of the gas film but did not affect the liquid film would increase the absorption of hydrogen chloride but would not affect the rate of oxygen absorption.

Changes in temperature influence several factors, and it is necessary to distinguish clearly between the effect of temperature on the equilibrium and its effect on the coefficients of diffusion. Increase in temperature makes the gas less soluble, thus tending to lower the rate of absorption. The diffusion coefficients themselves may, however, be either raised or lowered by temperature, depending upon the changes in film thickness and in specific

[1] The capacity coefficient k_G and similarly k_L may be defined as the specific coefficient of diffusivity divided by the effective film thickness, just as the capacity coefficient of heat transfer is looked upon as the specific thermal conductivity of the fluid divided by the effective film thickness. See pp. 134–158. The coefficient k_G of this chapter is identical with k of p. 459.

diffusivity. Liquid-film coefficients k_L rise rapidly with increasing temperature, both because of decreased film thickness due to lowered viscosity and because of greater diffusivities. On the other hand, data regarding effect of temperature on the gas film coefficient k_G are inconclusive, but the effect of temperature is not large, see p. 709. Although little is known regarding the effect of temperature on specific diffusivities through gas films, it seems probable that this effect is less than that due to an increase in the film thickness.

A type of apparatus in which gas bubbles up through a liquid would represent vitally different conditions from one where liquid drops are sprayed through a gas. In the first instance, a rising gas bubble would continuously expose fresh liquid surface and the conductivity of the liquid film would be high, whereas the gas film would be relatively undisturbed. Such a device should therefore be most satisfactory for absorbing the less soluble gases where liquid-film diffusion is controlling. In the other case, a falling drop might be expected to have only a very thin gas film but a fairly thick liquid film. Apparatus of a spray type will therefore, other things equal, be well suited for absorbing very soluble gases.

From these suggestions it is evident that the ratio of film coefficients (k_L/k_G) varies with the type of apparatus and with the conditions of operation. It is therefore quite possible that the absorption of a gas of intermediate solubility might be controlled primarily by liquid-film diffusion in one piece of equipment and by gas-film diffusion in another. This point is illustrated by the case of sulphur dioxide, which is almost entirely governed by the liquid film when passed over a free surface of liquid, but which is largely affected by the gas film when absorbed by bubbling through water.

It is possible to predict comparative performances of different solutes in the same equipment on the basis of this general concept. Under similar operating conditions the effective film thicknesses will in most cases be independent of the solute that is being absorbed.

For low concentrations of the diffusing gas there is a definite relationship between the coefficient k_G and the molecular weight M_G of the diffusing gas. For the units tabulated on page 661, this relationship requires that k_G be *directly* proportional to the

square root of M_G.[1] The molecular weight M_i of the inert gas and the partial pressure of the inert gas p' are involved in such a way that k_G varies *inversely* as the square root of M_i and inversely as p'. Furthermore, for different diffusing substances, the influence of such variables as velocity, temperature, and the like must be identical (see pp. 709 to 712).

Our knowledge as to liquid-film coefficients is incomplete. It is known that as the molecular weight of the diffusing material becomes high its diffusivity increases,[2] but the data show clearly that the change in diffusivity is small compared with that in molecular weight. In the absence of more definite information, it is assumed that, for the units here employed, the liquid-film cofficient k_L, under conditions of equal film thickness, is the same for all substances. This approximation is somewhat justified by the fact that diffusivity data given in the literature show a surprisingly small variation for various electrolytes and other aqueous solutions of low molecular weight.

Further data regarding factors affecting the capacity coefficients are given on pages 705 to 715.

Table of Nomenclature

W = Weight of solute in grams.
θ = Time in hours.
$\frac{dW}{d\theta}$ = Rate of absorption, in grams per hour.
S = Area of liquid-gas interface, in square centimeters.
k_G = Individual diffusion coefficient through gas film.
k_L = Individual diffusion coefficient through liquid film.
P = Partial pressure of solute in gas, in atmospheres.
C = Concentration of solute in liquid in grams per cubic centimeter.

Subscript G applies to conditions in main body of gas.
Subscript i applies to conditions at liquid-gas interface.
Subscript L applies to conditions in main body of liquid.

[1] However, if k_G be expressed in *mols* per unit time per unit interfacial area per unit driving force, in atmospheres, k_G varies *inversely* as the square root of M_G.

[2] Where diffusivity is expressed in mols, diffusivity decreases with increase in molecular weight of the diffusing substance.

H = Solubility coefficient = liquid concentration in grams per cubic centimeter divided by equilibrium gas pressure in atmospheres.
K_G = Overall diffusion coefficient, based on ΔP.
K_L = Overall diffusion coefficient, based on ΔC.
M = Molecular weight of solute.

2. Fluids and Solids

In the majority of cases solid absorbents pick up gases by adsorption, the equilibria being of the type shown in Figs. 165 and 166. The data available on adsorption rates are incomplete, but the indications are that the mechanism is one of gas-film diffusion, the film being, however, not merely on the outside of the grain but also to no small degree within the core. Consequently there is a very definite limit to the possibility of reducing the gas-film resistance by high gas velocity past the adsorbent.

The reason lies in the structure of solid adsorbents. Thus the individual grain of activated charcoal is not a dense solid, but is permeated by a labyrinth of exceedingly fine capillaries upon the walls of which the adsorbed gas is held (see p. 647). It has been estimated that in the case of highly activated charcoal the active surface of these capillaries is of the magnitude of 20 acres to the pound. Gas is adsorbed not merely in those capillaries near the outer surface of the grain, but in the inner ones as well. To penetrate the grain, however, the entering gas must diffuse along the capillaries, and this, rather than diffusion through the gas film around the outside of the grain as a whole, offers the major resistance to rapid adsorption. This resistance increases as adsorption proceeds, for at the start the entering gas is adsorbed and held at the very mouths of the capillaries, whereas later increments of gas adsorbed must diffuse down the capillaries, past the outer layers of carbon surface already saturated, to points located progressively deeper in the grain and not yet loaded up with gas. In the case of gases and vapors, however, this diffusion is rapid; so much so, that for small grain sizes, equilibria rather than adsorption rate is often the controlling factor in the process.

In the adsorption of materials from liquid solutions by solid adsorbents, the situation is very different. While the capillary

structure of the adsorbent granule remains the same, these capillaries in the interior of the grain are normally ineffective, because the material adsorbed from liquids almost always possesses very high molecular weight. For example, the organic color removed from sugar syrups by bone char and from oils by fuller's earth is in both cases complex in structure and colloidal or semi-colloidal in character. In consequence, the diffusion rate through the capillaries is exceedingly slow and, indeed, the indications are that the capillaries act in a certain sense as filters, their mouths on the outer surface of the grain becoming choked with adsorbed color.

There are two important consequences: In the first place, when the mouths of the capillaries reach equilibrium with the color concentration in the external solution, further adsorption becomes exceedingly slow, despite the fact that the total adsorptive capacity of the grain has been only partially utilized. In other words, there develops a false equilibrium, which, however, sets a practical limit to the adsorptive capacity of the solid. It is this false equilibrium in which the engineer is interested and which must be experimentally determined as the basis for computations and design. In the second place, the total effective adsorptive capacity of the solid is proportional, not to the total surface of the capillaries (*i.e.*, to the total weight of the solid), but rather to the surface of the grains themselves, because the effective capillary surface is limited to that in a thin layer below the outer surface of the grain. Thus, whereas it has been found experimentally that grinding 20-mesh carbon to particles less than 0.001 mm. in diameter increases the total adsorptive capacity for gases only 8 per cent, the capacity of similar solids for decolorization is approximately proportional to the total grain surface exposed, *i.e.*, for a given weight of adsorbent, inversely proportional to the average grain size (see p. 671). Consequently, while it is advantageous to use solid adsorbents for gases in the form of coarse grains, because this avoids the evils of dusting and high-pressure drop without introducing serious concomitant disadvantages, when employing similar adsorbents for liquids, the use of them in the form of relatively fine powders greatly increases both adsorbing capacity and rate per unit weight of adsorbent employed.

While from the preceding discussion it is obvious that the mechanism of diffusion of a solute from a liquid into a solid

adsorbent is complicated and, even for the same concentration difference, will be more rapid at the start of the adsorbing process than toward its end, none the less the data indicate that the adsorption rate is substantially proportional to the total surface of the adsorbing grain and to the difference in concentration between that in the solution around those grains and that in a solution in equilibrium with the material already adsorbed.

Because the total adsorptive capacity of the material is proportional to its surface rather than to its weight, the determination of the adsorption equilibrium is very unsatisfactory. It is difficult to get two samples of material of the same grain size and the same size distribution. Indeed if one take a granular material and separate it into two parts, there is a very marked tendency towards segregation of grains of varying size, and of these two samples the one with the smaller average grain size will have both the higher adsorptive capacity and the higher adsorption rate. Added to this is the still greater difficulty of duplicating the quality of an adsorbent in the preparation of separate samples. Thus, in the activation of charcoal by selective oxidation, it is difficult, if not impossible, to carry the activation to exactly the same point in successive runs. Obviously, in the regeneration of old adsorbent for re-use, as is practiced in the reactivation of charcoal, bone char and fuller's earth by furnacing, the chances for variation in quality of product are even greater. Because of these facts it is difficult to get satisfactory experimental checks in determination of either equilibrium or rate. In practice, it is best to secure both figures from analysis of operating data under plant conditions, but it is imperative to make sure that the data obtained are representative, by using the results of a larger number of tests. Furthermore, in employing such data as the basis for design, liberal factors of safety must be used.

CHAPTER XIX

ABSORPTION AND EXTRACTION

PART I. METHODS OF OPERATION: EQUIPMENT

1. Treatment of Gases by Liquids (Gas Washing and Scrubbing).—Efficient absorption from gases by liquids demands both counter-current flow and large interfacial contact between the phases (see pp. 574 and 635). The problem is entirely analogous to that arising in rectification, and the apparatus employed in that art is also frequently used in absorption (see pp. 574–578). Attention should be called to the fact that filled towers give less efficient contact than bubble-plate columns but possess the advantages of much less back pressure and smaller liquid content. The latter advantage may be particularly important where frequent starting and stopping is necessary. All filled towers, however, are likely to channel badly, especially at low liquor rates; and under this condition contact is lost because only a small fraction of the surface is properly wetted. In consequence filled towers are unsatisfactory where under operating conditions the rate of liquid flow is subject to wide variations (see p. 577).

Many types of tower filling are available. Thus, columns packed with coke are employed in the absorption of CO_2 from flue gas in bicarbonate solutions; slat-packed towers are sometimes preferred for absorption of light oil in mineral seal oil; packings of quartz, earthenware, and tile are valuable for acid liquids, and perforated sheet metal is also used in various cases. In absorbing light naphtha in suitable hydrocarbons, as in the washing of refinery gases, horizontal screens may be placed in a vertical column to expose fresh surfaces of the oil flowing down the tower.

Spray chambers of the type shown in Fig. 104 (p. 463) may be used for absorption, but where liquid is recirculated through the sprays, it is necessary, to obtain an approach to counter-flow of gas and liquid, to employ a number of chambers in series.

Figure 107 (p. 474) shows the Maclaurin centrifugal scrubber as utilized in absorption. The Ceco spray device secures contact

between gas and liquid by feeding the liquid upon a revolving disk. Figure 170[1] shows a section of the B. H. washer, a recent modification of the Fels scrubber, designed to give a contact between liquid and gas which is independent of the net flow of liquid through the tower. This type is especially suited to cases where extensive contact is required and the amount of liquid is small, as in absorbing very soluble gases. Within limits the amount of contact can be controlled by regulating the speed of the shaft which rotates the inclined vanes attached thereto.

2. Treatment of Gases by Solids.—Whenever a fluid, gas or liquid, is to be treated by a solid, one is handicapped by the

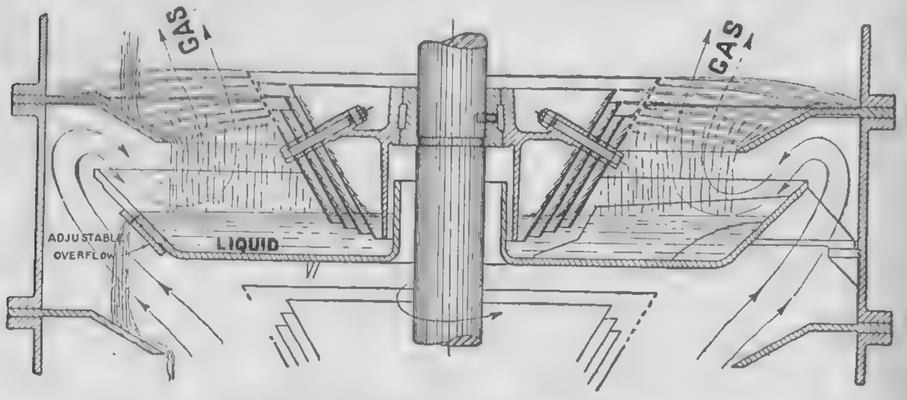


FIG. 170.—Longitudinal Section of Bartlett Hayward Washer.

difficulty of moving solids smoothly and continuously. This difficulty is so serious that it is the almost universal practice to place the solid in position and pass the fluid over it, leaving the solid undisturbed until its interaction with the fluid is complete. Thus, in the absorption of gasoline from natural gas, the absorbent charcoal in granulated form is packed in cylindrical containers several feet deep, through which the gas to be treated is allowed to flow. Three of these cylinders are operated together, the gas first entering a cylinder partly saturated with gasoline from previous treatments and flowing thence to a cylinder recently stripped of its gasoline content. The third cylinder is out of the gas circuit, in process of being stripped of its gasoline content by passing superheated steam through it. The mixture of gasoline vapor and steam leaving this cylinder is condensed and the gasoline recovered by decantation. When the charcoal in the first

[1] Courtesy, Bartlett Hayward Company, Baltimore, Md.

cylinder in the gas circuit becomes saturated with gasoline, it is cut out, the gas now entering what was previously the second cylinder in the line and flowing thence to the gasoline-free charcoal in the third cylinder, now stripped of its gasoline. The cylinder cut out of the line is then subjected to the stripping operation. It is thus seen that the plant operation is divided into three cycles, at the end of which conditions return to those originally obtaining. By this means the charcoal is used repeatedly with no physical movement or handling so long as it remains in process; this has the important advantage of lessening deterioration and loss of char by dusting. Such an operation is described as semi-continuous and represents two stages of counter-current action. As many stages may be introduced as desired, the use of less than three being unusual. This system of operation involves the same principle employed in rectification (p. 574), counter-current drying (p. 499), and counter-current transfer of heat (p. 173), but the principle is applied as in the operation of the ring furnace (p. 232).

Attempts have been made to secure a continuous movement of the solid treating agent in a direction opposite to that of the fluid treated. For example, it has been proposed to employ a traveling belt or screen to carry the solid, in an apparatus analogous to the band-type drier used for soap (see Fig. 113, p. 496). For solids which do not dust easily, the so-called "Jacob's Ladder" type of apparatus has been suggested, in which the solids slide down over a series of inclined shelves alternately projecting from the sides of a vertical container. Another proposal is that the gases be brought into contact with the pulverized solid, in a stepwise counter-current apparatus involving dust collectors and bag filters.

3. Treatment of Liquids by Gases or Vapors (Stripping or Denuding).—These operations are carried out in the same types of apparatus as described above for the treatment of gases by liquids. A familiar illustration is the stripping of benzene from absorbent oil, accomplished by blowing steam up through a tower at the top of which oil to be treated is fed. The benzene-free oil leaving the bottom is cooled before returning to the absorption tower, and for this purpose heat exchange is generally employed so far as practicable. The mixture of benzene vapor and steam leaving the top is condensed and the benzene is

separated by decantation. In order thoroughly to strip the oil and at the same time conserve steam, the temperature must be maintained high. If this be done by the condensation of live steam alone, the temperature limit is that corresponding to the pressure of steam in the stripping tower, *e.g.*, at atmospheric pressure to about 212° F. There is no need to adhere to this temperature limit, and less steam is required as the temperature is raised. The column should be heated, usually by steam condensing under pressure in closed coils. The temperature in the lower part of the column can be raised above that at the top of the column, even though a certain amount of vaporization of the absorbent oil results, since this vaporization can be rectified out in the upper part of the column by the refluxing action of the feed or, if desired, by the use of a refluxing section above the feed plate. It is important to realize that the closed coils used for heating should be distributed throughout the column below the feed plate, in proportion to the heat consumption due to vaporization and rise in temperature occurring in each section. A further large saving in the live steam injected directly into the column may be made by applying vacuum (see pp. 567–569). If one wish, the whole separation may be made by ordinary rectification, but the temperature required at the bottom of the still may cause decomposition.

4. Treatment of Liquids by Liquids.—These operations are usually carried out in tanks, provided with the proper auxiliaries to prevent loss of solvent, if volatile, with agitating devices of various types for securing intimate contact. After the treating agent has extracted its quota of material, the agitation is discontinued and the two layers are separated by decantation (see pp. 332–333).

5. Treatment of Liquids by Solids.—Where necessary to remove a component from solution in a liquid by means of a solid adsorbent, the classical method is to allow the liquid to flow through a deep bed of the adsorbent in granular form. The mass is called a percolation filter, although the mechanism of removal is in no sense filtration, the voids between the grains of the adsorbent being far too large to prevent the passage of the largest particles of the solute. The mechanism of removal is pure adsorption (see pp. 643 to 649).

Counter-current flow is desirable, but study of the equilibria relationships (see Fig. 194, p. 719) makes it clear that the more intense the adsorption (*i.e.*, the greater the value of n in the Freundlich equation, p. 645), the less the advantage of counter-current flow over batch operation. Consequently, such filters are frequently employed in single units, the solutions flowing through them until the concentration of the effluent liquor is no longer satisfactory. Where liquids of varying initial concentration are available for treatment, a filter is frequently employed first for weak liquors and later for stronger ones, without attempt to make the flow positively counter-current. The flow is usually by gravity. Whether the liquid should flow upward or downward depends upon the change of density produced by the adsorption; if treatment makes the liquid lighter, it should flow upward and if heavier, downward, in order to avoid the mixing by convection currents of purified liquid with impure material in earlier stages of filtration. Because the rate of adsorption is very small (see p. 663), time must be allowed; *i.e.*, flow of liquid through the filter must be slow. It is frequently possible to increase the adsorption rate by increasing the temperature of the operation, the increased rate of diffusion more than compensating the decreased affinity of the adsorbent for the solute.

By far the most serious difficulty encountered in the operation of percolation filters is channeling. It is impracticable to produce a granular adsorbent of absolutely uniform grain size and shape, and when charging the filter the tendency for segregation of granules of varying size is marked, the more so the greater the variation in size. Thus, if the material entering the filter be discharged at any given point, a cone is built up at that point and the larger granules roll to the bottom, while the core of the cone consists of the finer particles. If the adsorbent be fed to the middle of the filter, this segregation of large particles at the side is very serious. This coarse material offers far less resistance to flow of liquid; hence the major portion of the liquid goes through this section and the flow through the finer material is negligible. Various mechanical devices have been tried for securing uniform distribution of the granules while charging the filter but, though it is possible to localize segregation, it is difficult to eliminate it altogether. So long as segregation is sufficient to offer through the filter some path of relatively low resistance to liquid flow,

channeling occurs and the utilization of the adsorbent is greatly impaired, because the liquid fails to flow through the finer material, which is most efficient from the point of view of both capacity and rate.[1] Where the adsorption produces in the liquid an appreciable change in gravity, the evils of channeling may be reduced to a minimum by using such low liquor velocities that the differences in liquor gravity developed by the adsorption itself maintain uniformity of liquor concentration at each horizontal section through the filter. Thus, assume that adsorption decreases the density of the liquid. In such case the liquid should obviously flow upward through the filter. At the start the liquid at any particular horizontal level in the bed tends to flow predominantly through the coarse material, but this soon saturates that material and consequently there is no further decrease in density of this liquid. This develops an additional pressure head, which does not exist through the fine material, in which, due both to the smaller liquor flow through it and to its greater adsorptive capacity, adsorption and consequently decrease in density have gone much further. Hence, there is developed a greater pressure gradient through the fine material than through the coarse, and, provided the velocity is sufficiently low so that the greater friction through the fines does not overbalance this excess-pressure gradient, the liquid will now flow predominantly through the fines. Unfortunately, however, in the majority of cases the change in density due to adsorption itself is too small to make this method of overcoming the evils of channeling effective.

Percolation filters are frequently employed for removing from liquids or solutions a relatively small amount of impurity, as, for example, in the decolorization of oils by fuller's earth or of sugar syrups by bone char. When the adsorbent has become saturated, it is obvious that the liquid held in its voids, both those between the grains and the capillary spaces within the grains themselves, must be recovered. From the voids between the grains a certain amount can be removed by draining the filter. The rest is usually removed by washing; in the case of oils this may be done with petroleum ether, and of sugar syrups with water. The wash liquid is usually lower in density than the liquid under treatment, and consequently downward flow should

[1] See p. 663.

be employed to prevent convection. It is frequently best not to drain the filter before starting the washing operation, since otherwise a great deal of unnecessary mixing results, due to the rush of the washing liquid applied to the top of the filter down through the empty voids between the grains. The rate of washing should be low, particularly at the start, so that the heavy liquid, even that entrapped in the capillary voids within the grains, may flow down and out from the filter ahead of the wash liquid, which follows it through the filter like a piston. In so far as this piston action is effective, it results in removal of the original liquid without dilution with the wash liquid, but the final removal is always by diffusion and is correspondingly slow.

The wash liquid is almost always removed from the adsorbent by evaporation. In the case of water, the adsorbent is usually removed from the filter and dried; in the case of organic solvents, such as petroleum naphtha, the solvent is usually vaporized by blowing in steam, the vapors going to a suitable condenser for recovery. It is frequently possible to revivify or reactivate the adsorbent. Thus, in the adsorption of organic color by bone char and fuller's earth, these materials are ignited to a moderate temperature in the presence of a certain amount of air. This chars the color which was adsorbed, burning out a certain amount of it and converting the residue into a carbon which is itself decidedly adsorbent. It is thus possible to re-use the material a large number of times. In the case of the bone char, the limit to the life of the adsorbent is often dusting, but the fuller's earth becomes less effective with revivification and is seldom employed more than ten to fifteen times. After furnacing, the adsorbent must, of course, be cooled and reintroduced into the filter.

The potential advantages of increasing adsorbent capacity and adsorption rate by the use of finer granules are very attractive, but fine material clogs the percolation filter. The possibility of securing the necessary contact between solid and liquid by agitating the adsorbent in the liquid in the form of very fine granules and separating the adsorbent after saturation by filtration is obvious, but before the development of the modern leaf and rotary filters, the filtering operation was too expensive to make this method practicable. In recent years, however, the method has come into widespread use. The rotary filter has proved best suited to the purpose. The grain size of the

adsorbent must not be so small that the filtration rate is seriously reduced or that dusting develops in any subsequent operations, such as revivification. The smaller the amount of adsorbent relative to the volume of liquid treated, the simpler and more efficient is the process. Hence, this method is particularly advantageous when employing treating agents of high adsorbent capacity such, for example, as activated charcoal. Unfortunately, in this system the advantages of counter-flow can be secured only at the expense of multiplicity of operations. In practice one seldom employs more than one or at the most two agitations with a given body of liquid. However, where adsorption is marked, *i.e.*, the value of n in the Freundlich equation is high, the advantages of counter-current action are far less than where adsorption is low (see pp. 718 to 720).

Systematic sedimentation (see p. 675) offers certain obvious advantages for this treatment of a liquid by a solid and will sometimes commend itself. Sedimentation is impossible under conditions of violent agitation, however, and for adsorption filtration agitation is very essential because of the extremely high molecular weight and correspondingly low diffusion rate of the material removed from the solution (see p. 663). Consequently, therefore, agitation followed by mechanical filtration of the solid from the liquid in which it is suspended is usually the better method.

6. Treatment of Solids by Gases or Vapors.—The operation is the reverse of the treatment of vapors by solids and the principles governing it are identical. Furthermore, because of the difficulty of handling the solids, it is usually conducted in the same container used for the original adsorption. The removal will be the more complete the larger the amount of gas swept over the solid and the higher the temperature. In the case of adsorbed organic liquids, the best treating agent is steam, because, by condensing both it and the adsorbed vapor, the two can be separated by decantation. It is obviously desirable to keep the amount of steam necessary for treatment down to a minimum, and this can be done by raising the temperatures. Most solid adsorbents, however, are very poor conductors of heat, and the problem of distributing the heat throughout the adsorbent is a very real one. Sometimes coils are imbedded in the adsorbent, for water cooling during the adsorption phase

of the operation and steam heating during the stripping. The danger of leakage is serious, and the coils should be so constructed that, where necessary, leaky units can be shut off without stopping operation. Where the concentration of vapor adsorbed is high, cooling units of this sort are often essential during the adsorption operation, since it would otherwise be impossible to dissipate the heat, but where the adsorbent is dilute, *i.e.*, under those conditions for which solid adsorbents are peculiarly advantageous, the heat capacity of the diluent gas is enough to prevent serious temperature rise during adsorption. In stripping it is usually best to supply the necessary heat in the form of highly superheated steam. This has the advantage that the very flow of the steam itself distributes the heat perfectly throughout the adsorbent mass, despite its poor heat conductivity. Furthermore, during the evaporation of the adsorbed vapor from the solid, the heat absorption lowers the temperature of the steam, while as soon as stripping is complete, the temperature of the steam leaving the unit rises substantially to that at entrance. This gives a convenient and dependable control of the stripping operation. After stripping, the adsorbent mass can be cooled by blowing through it cold air or inert gas.

Toward the end of the stripping operation it is obvious that a unit amount of steam can remove but little adsorbed vapor, because of the low partial pressure of the latter. Such steam still possesses a large vapor-carrying capacity, which can be utilized by allowing the steam to flow through a number of containers in series. Due to the complications involved, however, this is seldom done.

7. Treatment of Solids by Liquids (Lixiviation or Leaching).—The technique of the art of lixiviation was developed in connection with the leaching of tannin from various barks and in similar important processes, and led to the adoption of what has been described above as a stepwise, counter-current system. In the extraction of solids by liquids it is called the Shank's system. In the common case where water is used as the treating agent, the fresh bark is treated with a solution already rich in tannin, while the exhausted bark is given a final wash with fresh water. In Shank's system the solid to be extracted is charged into large tanks, where it remains undisturbed until the extraction is completed, then to be replaced by fresh charge. Where necessary,

the charge is first broken up into granules. The grain size should be as nearly uniform as possible, since for large lumps extraction is slow, whereas fine material packs and interferes with flow of liquid through the mass. For the reasons given on page 669, in charging the tanks precautions should be taken to prevent segregation of particles of varying size, though usually the change of density of the liquid as extraction proceeds is sufficient to overcome this evil if rate of flow is slow (see p. 670). Since the liquid almost always increases in density, the flow is downward. The tanks are usually arranged in parallel rows, similar in principle to the arrangement of the cells in a ring furnace (see p. 230). They should obviously be identical in size and level. The water or other lixiviant enters the most nearly exhausted tank of the series, flows down through it, and thence up to the top of the next tank in order.

Where gravity head is used, there must be a difference in liquid level between tanks sufficient to overcome the friction through the material, and, in addition, the head corresponding to the difference between the gravity of the effluent liquor from the tank and the average of that in the tank itself. Where the number of tanks in series is large, this difference in head becomes a serious factor, because the charge in the fresh tank must be covered with liquid and consequently the full depth of the tank cannot be utilized for charge. The lixiviant is usually employed hot, to increase both solubility and rate of extraction. Where extraction is slow, heat losses, not only by radiation and conduction, but also by evaporation, are sometimes serious.

A difficulty sometimes encountered is the packing of the charge due to its reduction by the extraction process itself to a finely subdivided residue. This is particularly likely to develop when the percentage of solute in the charge is high. Thus, in the manufacture of black ash in the LeBlanc process, it is essential to modify the composition of the charge to the black-ash furnace to secure a product which will, to a reasonable degree, retain a porous structure and mechanical strength as leaching proceeds. Fortunately, however, solids containing a high percentage of soluble matter can usually be leached by simple agitation, followed by separation of the residue by sedimentation.

The Shank's system was originally developed primarily because of the mechanical difficulties of moving solids under

proper conditions of control. This difficulty was avoided by leaving the solid stationary and letting all the movement, during the extraction process itself, be that of liquid past the solid. The advent of the modern developments in the mechanical conveying of solids obviously made possible a new technique in lixiviation. It became practicable to move both solid and liquid simultaneously, counter-current to each other, in intimate contact, independently of the state of subdivision of the solid. The Dorr classifier (Fig. 80, p. 326) consists essentially of a scraper conveyor which drags a granular solid up an inclined plane against a counter-current of lixiviant. The solid is fed at the lower end of the incline and is discharged at its top. While the motion of the scrapers is slow, none the less their agitating action is such that this type of equipment is not well suited for the treatment of finely subdivided, slow-settling solids. Furthermore, the agitation distinctly interferes with the counter-current action, due to the mixing of liquids at different points in the trough. This may be offset by using these units in series. The apparatus has large capacity and low operating cost. The grain size can be sufficiently small so that extraction is quite rapid. An important illustration is the leaching of copper salts from pyrites cinder.

For finer materials it is best to reduce the agitation to a minimum and to let the solid move through the liquid by gravity sedimentation. This is accomplished in the Dorr continuous thickener (Fig. 83, p. 339). The suspension is fed into the middle of the top, the clear decanted liquor overflows at the periphery, and a concentrated sludge is continuously removed from the bottom. There is no counter-current flow in a given unit, but the units may be successfully used in series. A typical application is found in the extraction of caustic soda from calcium carbonate sludge in the causticization of soda ash.

In principle the washing of a sludge in a filter comes under this heading. This has already been discussed in Chap. XI.

PART II. DESIGN: GASES BY LIQUIDS

In the absorption of gases by liquids the conditions of operation are usually counter-current and continuous or at least reasonably so over definite time intervals. Consequently the discussion

of quantitative methods of design will be restricted to such conditions.[1]

Figure 171 represents a counter-current absorption unit. The incoming gas is indicated entering at the bottom and leaving at the top and the liquid absorbent is flowing in the opposite direction. The entering gas carries the material to be absorbed, which dissolves as solute in the liquid absorbent. The exit gas carries only the residual solute not dissolved in the absorbent liquid flowing from the bottom. As in the case of calculations in Drying (pp. 441–458), it is advisable to express the concentrations of material being absorbed, *i.e.*, of solute as parts of solute per part of solute-free gas for the gas phase and parts of solute per part of solute-free absorbent for the liquid phase. Unless otherwise stated, both gas and liquid concentrations will be expressed as pounds per pound.[2]

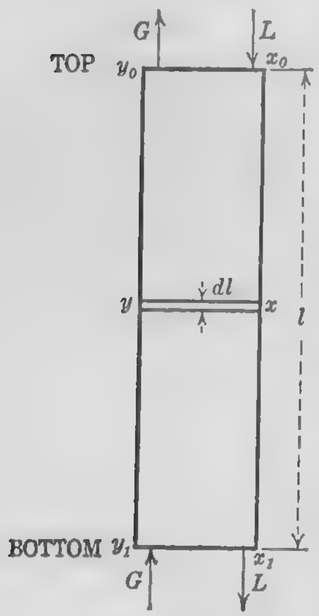


FIG. 171.

Call the pounds of incoming, solute-free gas per unit time G and the pounds of liquid absorbent L. The concentration of solute in the liquid, expressed as pounds per pound of absorbent liquid is x. This has the value x_1 at the bottom of the tower in the effluent liquid and x_0 at the top of the tower in the incoming liquid. y is the concentration of solute in the gas, expressed as pounds of solute per pound of solute-free gas. Its value is y_1 in the incoming gas and y_0 in the outgoing. Consider any section in the middle of the tower, taken at right angles to its axis. At this section the concentrations are x and y, the numerical values of these quantities differing of course with the point at which

[1] Computation methods adaptable to other cases will, however, be found on pages 715 and 721.

[2] Any quantity units desired can be used for each of the three components. Not infrequently the unit of gas quantity is 1,000 cu. ft. under some specified conditions of temperature and pressure. Sometimes the amount of solute in that gas is given in grains (ammonia in illuminating gas) and at others in gallons in the liquid state (benzene in the same gas).

the section is taken. Consider a second section at a differential distance dL below the first, at which point the corresponding concentrations are $x+dx$ and $y+dy$. Since equality of input and output demands that any solute removed from the gas in this section be taken up by the liquid, it follows that $Gdy=Ldx$. Furthermore, since continuity of operation is assumed, L and G are constants for any fixed conditions of operation. It is, therefore, possible to integrate this equation directly, obtaining $Gy = Lx+$ constant. This equality may also be written

$$G(y-y_0)=L(x-x_0) \quad \ldots\ldots\ldots \quad (1)$$

Inspection of this equation shows that in any such continuous, counter-current system, y must of necessity be linear in x. Because this relation was derived solely from an equality of input and output, it must hold whatever the character of the equilibria between the phases, the type of apparatus, the intimacy of contact, the relative velocities of flow or any other similar relationships however important from other points of view. It does, however, postulate steady rates of flow of both gas and liquid.

Minimum Ratio of Liquid to Gas.—As a specific case consider the drying of air by sulphuric acid. The equilibrium relationship between air and sulphuric acid is given by the curve $OABC$ in Fig. 172.[1] Obviously, sulphuric acid can absorb water only from air containing more than corresponds to this equilibrium; *i.e.*, any air being dried by sulphuric must correspond to points to the left of this curve. Furthermore, if one assume air entering such a system with a moisture content $y_1=0.016$ (Fig. 173) being treated with sulphuric with an initial moisture content $x_0=0.60$, the moisture in the air being ultimately reduced to $y_0=0.006$ and the water content of the acid rising to $x_1=1.4$, it follows from the preceding paragraph that the concentrations of moisture in both the air and the acid throughout the apparatus must be represented by the line EF. Such a line must always lie to the left of the equilibrium curve and furthermore it can never cross that curve although, theoretically at least, it can touch it. However, if it touches the equilibrium curve, tangentially or otherwise, at that point gas and liquid are at equilibrium or

[1] Based on data given by R. E. WILSON, *Jour. Ind. Eng. Chem.*, 13, No. 4 (April, 1921), 326.

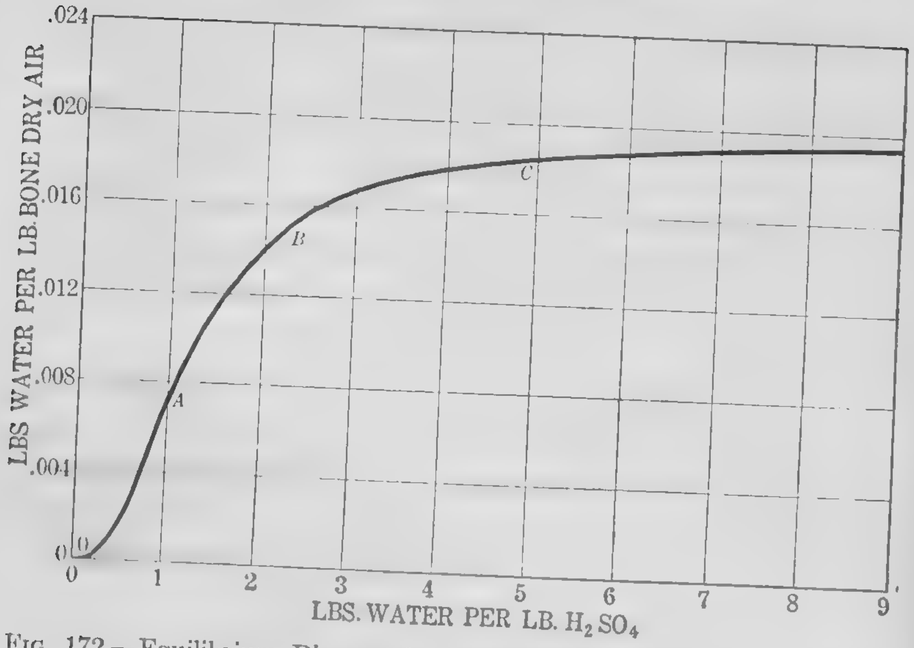


FIG. 172.—Equilibrium Diagram for Distribution of H_2O between Air and Sulphuric Acid. (Data Expressed in Stoichiometric Units.)

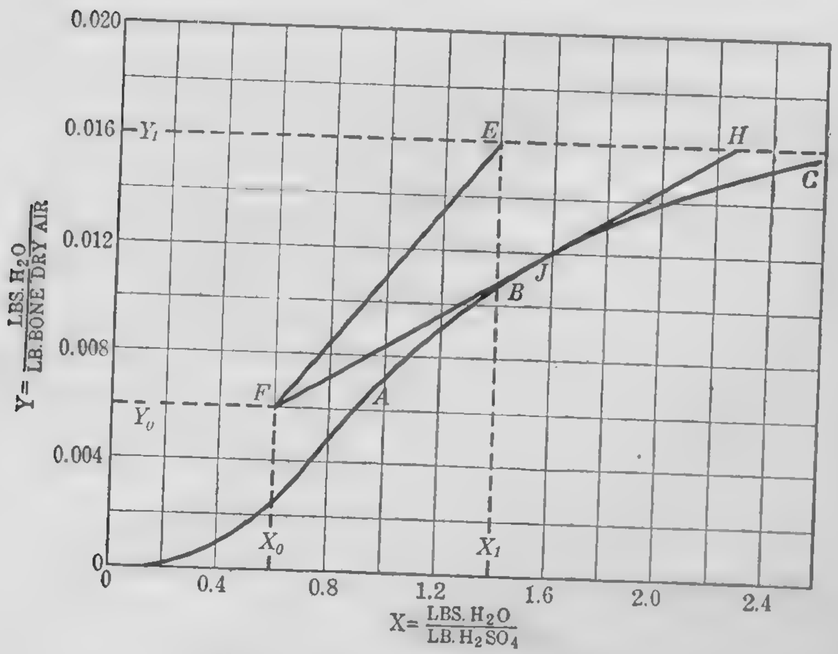


FIG. 173.—Absorption Diagram.

only differentially separated from it, so that transfer of solute from gas to liquid in the neighborhood of that point is indefinitely slow, requiring, therefore, indefinitely large surface of contact, which is equivalent to a negligible capacity for any apparatus of finite size.

Inspection of Eq. (1) shows that the slope of the line EF is the ratio of liquid absorbent to gas treated, in this case 0.0125 lb. of H_2SO_4 per pound of bone dry air. Since in general it is desirable to use as little absorbent as practicable, it is important to keep this slope low. Assume, for example, that it be required to dry air down to a moisture content $y_0 = 0.006$ with acid entering the system with a concentration $x_0 = 0.6$. This corresponds to point F on Fig. 173. The flattest line which can be drawn through F and reach the high water content $y_1 = 0.016$ without crossing the equilibrium curve is obviously the line FH, tangent to the equilibrium curve at J. The slope of this line $(0.016 - 0.006)/(2.26 - 0.6) = 0.006$ lb. of H_2SO_4 per pound of bone dry air therefore represents the smallest ratio of acid to air which it is theoretically possible to employ in drying air of high moisture content y_1 to the low moisture content y_0 by the use of acid with initial water content of x_0. Furthermore, since in such a system one would of necessity approach equilibrium in the middle of the absorber, it follows that the air-treating capacity of the absorber would be negligibly small or else the size of the absorber indefinitely great.

If, however, the initial air to be treated contain less moisture than corresponds to point J, it then becomes possible to draw flatter lines, *i.e.*, to use less acid per mol of air and still stay on the left of the equilibrium curve. This diagram therefore makes it possible for one to determine directly the theoretically minimum amount of liquid absorbent necessary for any particular case. It is obvious that the amount actually employed will of necessity exceed this minimum by a margin sufficient to furnish reasonable capacity.

ABSORPTION RATE

On pages 651 to 659 it was shown that the instantaneous rate of transfer of material from the one phase to the other is proportional to the surface of contact between the phases and to the concentration gradient through each of the two

surface films on the two sides of the interface, the two phases being at equilibrium at the interface itself. It therefore follows that in Fig. 173 the equilibrium curve *OABC* represents the interfacial conditions; *i.e.*, at each point in the apparatus the concentrations there existing at the interface must fall somewhere on this curve. Calling k_G and k_L the individual or film coefficients of the gas and liquid films respectively, A the area of cross-

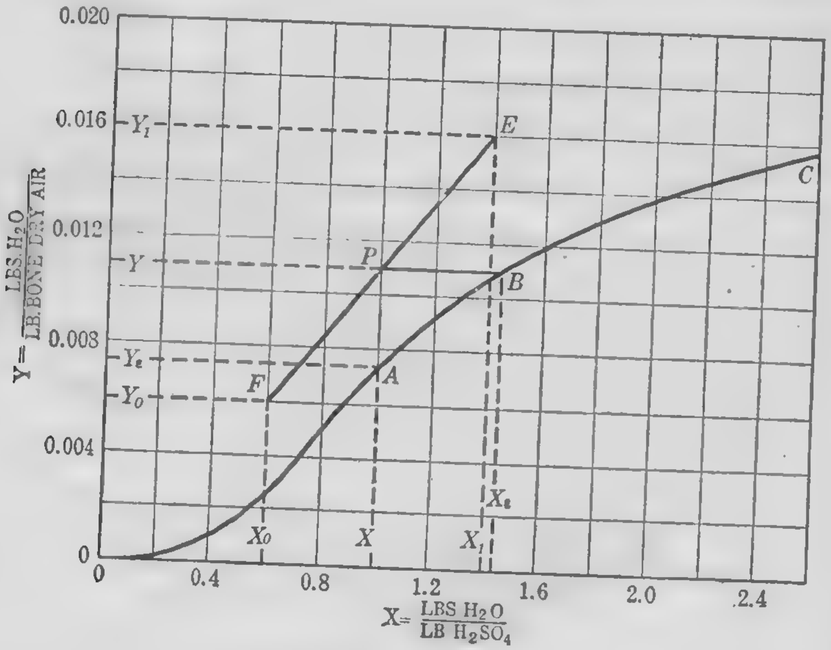


FIG. 174.—Absorption Diagram.

section of the apparatus, a the interfacial surface of contact between the gas and the liquid per unit volume of the apparatus,[1] and x_e and y_e the liquid and gaseous concentrations at equilibrium and therefore also at the interface, the rate of transfer of material can be expressed as follows:

$$\frac{dW}{d\theta} = Ldx = k_L aA(x_e - x)dl = Gdy = k_G aA(y - y_e)dl. \quad . \quad . \quad (2)$$

Liquid-film Controlling.—In Fig. 174 the equilibrium curve and the line FE of Fig. 173 are reproduced. The point P on the line FE represents the conditions in liquid and gas respectively at a certain point in the absorber, where the liquid and gas concentrations are x and y, respectively. Assume for the instant

[1] Obviously S, the total interfacial surface, equals aAl.

that in this particular case the diffusional resistance is mainly in the liquid film and that the gas-film resistance is negligible, *i.e.*, that the liquid film is the controlling factor (see p. 656). This is equivalent to saying that the concentration gradient through the gas film is negligible, or that the gas concentration at the interface is essentially identical with the concentration in the bulk of the gas y. It therefore follows that the interfacial

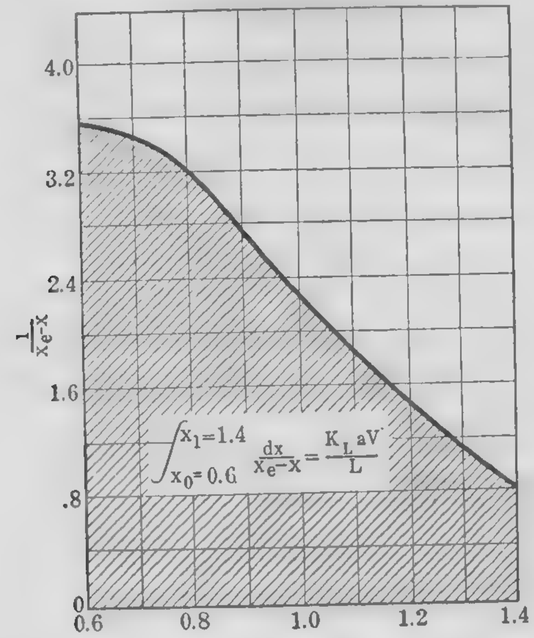


FIG. 175.—Graphical Integration, Liquid Film Controlling.

conditions are represented by point B in Fig. 174, at which the concentration in the gas film at the interface is equal to that in the main body of the gas, while the concentration in the liquid film at the interface has the value x_e. Therefore, the driving force causing diffusion in Eq. (2) is numerically equal to $x_e - x$, corresponding to the length of the line PB.

Rewriting Eq. (2) in the form,

$$\frac{dx}{x_e - x} = \frac{k_L aA\,dl}{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

it is seen that, granting a knowledge of the constants k_L, a, and A, one can calculate the length of absorber necessary by evaluating the integral, $dx/(x_e - x)$. This may be done by plotting the reciprocal of $(x_e - x)$ *versus* x. This has been done in Fig. 175 and

the cross-hatched area represents the value of the integral in question, and is numerically equal to $k_L aAl/L$. In this way it is possible to determine the volume of absorber necessary for any desired operation, once the constants of the equipment are known for the case in question.

Gas-film Controlling.—Assume, on the other hand, that this is a case in which the gas film is controlling, *i.e.*, in which the resistance of the gas film is considerable and that of the liquid film negligible (see pp. 655 to 656). Since the concentration in the liquid film at the interface will be substantially equal to that in the main body of the liquid x, it follows that the interfacial conditions will correspond to the point A (Fig. 174). Furthermore, the driving force causing diffusion through the gas film is $y-y_e$, corresponding to the line PA in Fig. 174. It is obvious that Eq. (2) can be graphically integrated for this case by a method entirely analogous to that given above, *i.e.*, by plotting $\frac{1}{y-y_e}$ *versus* y, the area under the curve being equal to $\frac{k_G aAl}{G}$.

Illustration 1.—In drying air for a certain process a sulphuric acid absorption tower is employed. The entering acid contains 90.8 per cent H_2SO_4 by weight, and its concentration drops to 47.6 per cent H_2SO_4 in passing through the tower. The air enters at 25° C. with a relative humidity of 70 per cent, and analysis of the effluent air shows 3.09 g. of moisture per cubic meter of bone-dry air at 25° C. and normal barometer. The tower is equipped with lead cooling coils to maintain it at substantially constant temperature throughout and operates at 25° C.

It is necessary to build a second tower for the same capacity as the present one, to meet the same operating conditions, except that the new tower is to be designed for a rate of flow of acid twice that now employed. What will be the necessary size of the new tower, expressed as a percentage of the size of the present tower?

Notes.—For equilibrium data, see Fig. 172 (p. 678). Vapor pressure of water at 25° C. is 23.76 mm. of mercury. The gas-film resistance may be assumed of controlling importance.

Solution to Illustration 1. *Present Conditions.*—The partial pressure of water vapor in the entering air is (23.76) (0.70) = 16.63 mm. of mercury.

$$y_1 = \frac{16.63\ (18.02)}{(760-16.6)\ (29)} = 0.0139 \frac{\text{Pounds water vapor}}{\text{Pound bone-dry air}}$$

$$x_1 = \frac{100-47.6}{47.6} = 1.10 \frac{\text{Pounds water}}{\text{Pound } H_2SO_4}$$

A cubic meter of dry air at 25° C. = 1,000 liters = $1{,}000\frac{273}{273+25} = 916$ liters at standard conditions of temperature and pressure. However, since

the gram molecular volume under these conditions is 22.4 liters and the molecular weight of air is 29, the weight of this air is 916(29/22.4) = 1186. Hence, the weight ratio of water to dry air is 3.09/1186 = 0.0026.

$$x_0 = \frac{100-90.8}{90.8} = 0.101 \frac{\text{Pounds water}}{\text{Pound } H_2SO_4}$$

Figure 176 shows the operating line, based on these coordinates, plotted on the equilibrium diagram.

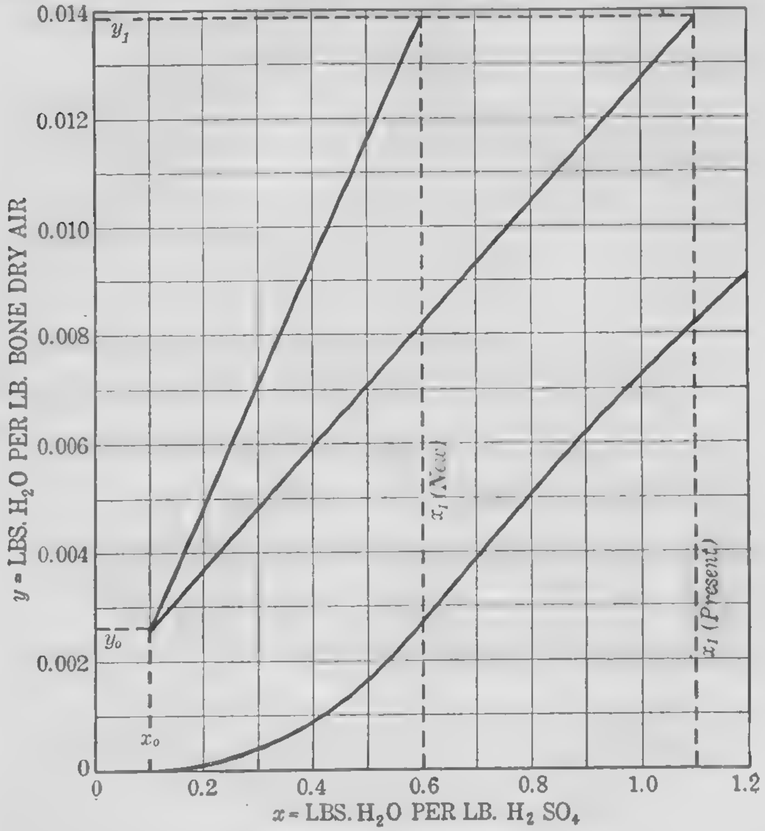


FIG. 176.—Absorption Diagram for Problem 1.

The following table gives the value of y_e corresponding to values of y as read from Fig. 176, based on the operating line for the present tower.

y	y_e	$y-y_e$	$\frac{1}{y-y_e}$
0.0026	0	0.0026	384
0.0036	0.0001	0.0035	285
0.00582	0.00082	0.0050	200
0.0081	0.0026	0.0055	182
0.0104	0.00501	0.00536	187
0.01268	0.00726	0.00542	185
0.01390	0.00822	0.00566	177

In Fig. 177 the values of $1/(y-y_e)$ are plotted *versus* y for values of y from 0.0026 to 0.0139.

The area under the curve BC is 46.1 squares. Each square is (50) (0.001) = 0.05 units; hence the area is 2.31 units, *i.e.*,

$$\int_{y_0=0.0026}^{y_1=0.0139} \frac{dy}{y-y_e} = 2.31 = \frac{K_G a A l}{G} = \frac{K_G a V}{G}$$

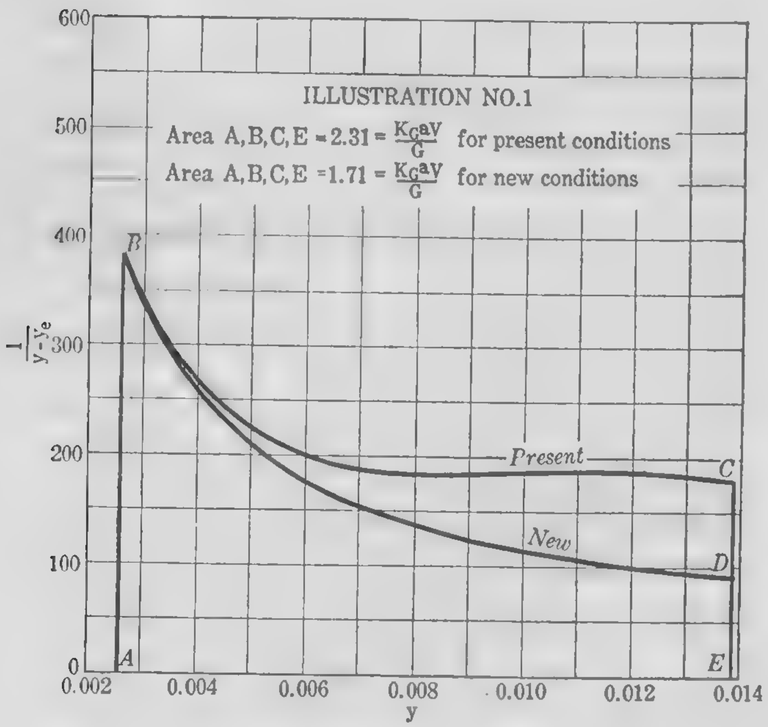


FIG. 177.—Graphical Integration, Gas Film Controlling.

New Conditions.—The slope of the operating line equals pounds of H_2SO_4 per pound of bone-dry air. The operating line for the new conditions will have a slope twice as high as in the present tower.

$$\text{Slope for present conditions} = \frac{0.0139-0.0026}{1.10-0.101} = 0.0113.$$

$$\text{Slope for new conditions} = \frac{0.0139-0.0026}{x_1-0.101} = 0.0226,$$

whence $x_1 = 0.601$.

Figure 176 also shows the operating line for the *new* tower. The following table gives the values of y_e corresponding to various values of y as read from Fig. 176, based on the operating line for the new tower.

y	y_e	$y-y_e$	$\frac{1}{y-y_e}$
0.0026	0	0.0026	384
0.00465	0.0001	0.00455	220
0.00695	0.00035	0.00660	152
0.00925	0.00082	0.00843	119
0.01155	0.0016	0.00995	101
0.0139	0.0026	0.01123	89

These values of $1/(y-y_e)$ for the new tower have been plotted *versus* y in Fig. 177, for values of y from 0.0026 to 0.0139.

The area under the curve BD is 34.2 squares. Since each square is (50) (0.001) = 0.05 units, the area is 1.71 units = $K_G a A l/G$.

Inasmuch as the exact effect of gas velocity on $K_G a$ for this case has not been determined, the gas velocity G in the new tower will be made the same as in the present tower, requiring the same value of the cross section A as at present.

Hence $$\frac{l_{\text{new}}}{l_{\text{present}}} = \frac{(1.71G/K_G a A)_{\text{new}}}{(2.31G/K_G a A)_{\text{present}}} = 0.74.$$

Therefore, the height of the new tower should be 74 per cent of the height of the present tower.

Illustration 2.—In drying air for a certain process a sulphuric acid counter-current absorption tower is employed. The entering acid contains 90.8 per cent H_2SO_4 by weight and its concentration drops to 46.6 per cent H_2SO_4 in passing through the tower. The air enters at 25° C. with a dew point of 13.0° C., and analysis of the effluent air shows 3.09 g. of moisture per cubic meter of bone-dry air at 25° C. and normal barometer. The tower is equipped with lead cooling coils to maintain it at substantially constant temperature throughout and operates at 25° C.

Suppose that the entering air should increase in moisture content: the worst possible case would be for the air to enter saturated at 25° C. For this case, without changing the tower, would it be possible to reduce the moisture content of the effluent air to the same value as before? If so, how much acid would have to be used?

Notes.—For the equilibrium curve at 25° C., see Fig. 172 (p. 678). Barometer 760 mm. of mercury.

Vapor tension of water at 25° C. is 23.7 mm. Hg., and at 13.0°C., 11.23 mm. The gas-film resistance may be assumed of controlling importance.

Solution to Illustration 2. *Present Conditions.*—Since the entering air has a dew point of 13.0° C., at which temperature the saturation pressure of water is 11.23 mm. of mercury,

$$y_1 = \frac{(11.23)\ (18.02)}{(760-11.23)\ (29.0)} = 0.0093 \text{ lb. water vapor per pound of dry air.}$$

Also from the humidity chart, Fig. 102 (p. 448), the humidity of air with a dew point of 55.4° F. (13.0° C.) is found to be 0.0093 lb. of water per pound of dry air.

$$y_0=\frac{(3.09)\ (0.0283)\ (359)\ (298)}{(454)\ (29)\ (273)}=0.0026\ \frac{\text{Pounds } H_2O}{\text{Pound dry air}}.$$

$$x_0=\frac{100-90.8}{90.8}=0.1013\ \frac{\text{Pound } H_2O}{\text{Pound } H_2SO_4}.$$

$$x_1=\frac{100-46.6}{46.6}=1.145\ \frac{\text{Pound } H_2O}{\text{Pound } H_2SO_4}.$$

These coordinates determine the operating line, which is plotted in Fig. 178 on the equilibrium diagram.

By Eq. (2), $G\,dy=K_Ga\,A\,dl\ (y-y_e)$. Hence,

$$\int_{y_0}^{y_1}\frac{dy}{y-y_e}=\frac{K_GaAl}{G}=\frac{K_GaV}{G}.$$

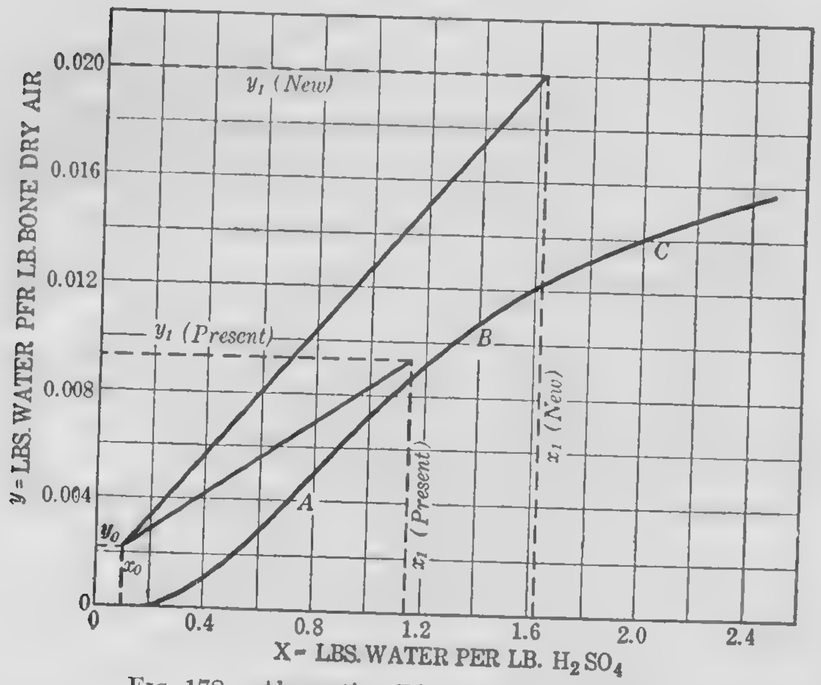


FIG. 178.—Absorption Diagram for Problem 2.

The following table shows the values of y_e corresponding to the various values of y, as read from Fig. 178.

y	y_e	$y-y_e$	$\frac{1}{y-y_e}$
0.0093	0.0086	0.0007	1430
0.0083	0.00726	0.00104	962
0.0070	0.00503	0.00197	507
0.00573	0.0026	0.00313	320
0.00422	0.00083	0.00339	295
0.00360	0.0001	0.00350	285
0.00260	nil	0.0026	384

In Fig. 179, the values of $1/(y-y_e)$ are plotted *versus* y for values of y from $y=0.0093$ to $y=0.0026$.

The area[1] under the curve is $3.3=\frac{K_GaAl}{G}=\frac{K_GaV}{G}$.

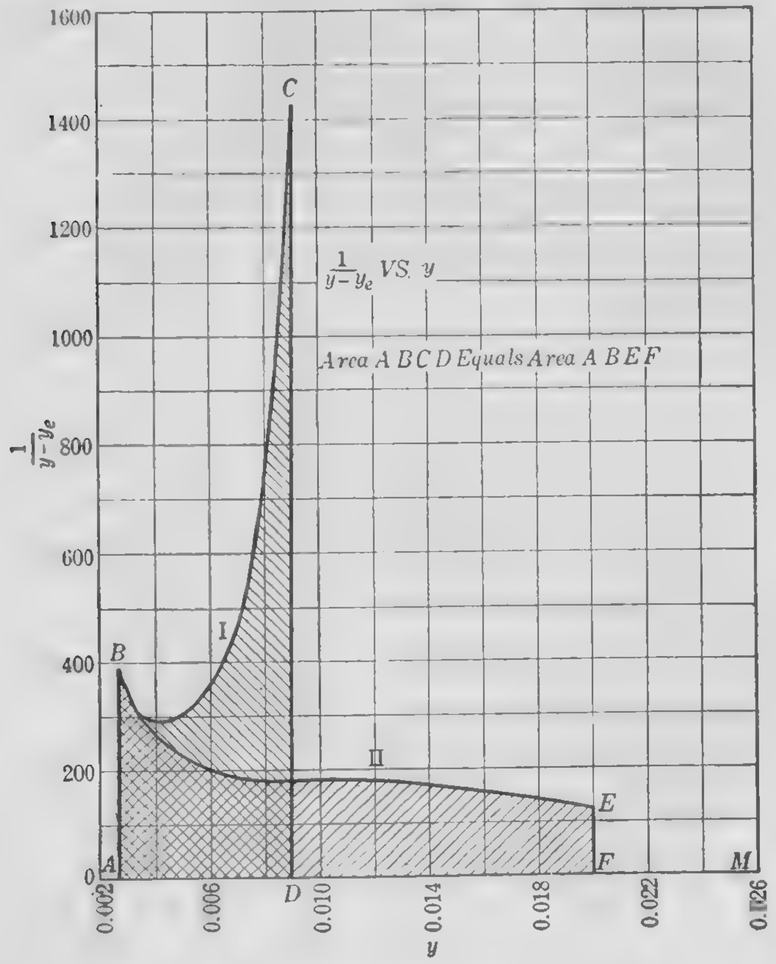


FIG. 179.—Graphical Integration for Problem 2.

New Conditions.

$$y_1=\frac{(23.7)\ (18.02)}{(760-23.7)\ (29)}=0.020\ \frac{\text{Pounds } H_2O}{\text{Pound dry air}}.$$

$y_0=0.0026$ as before.

$x_0=0.1013$ as before.

Since the tower itself and the flow of dry air remain unchanged, the values of K_Ga, A, and G are unchanged; therefore, the area K_GaAl/G must remain constant. The new limits of y are known to be 0.020 and 0.0026. The operating line must pass through the point $x_0=0.1013$, $y_0=0.0026$. A

[1] The area is 16.5 squares, and since each square equals (0.002) (100) = 0.2 unit, the area equals 3.3.

value of x_1 is assumed, and the corresponding values of $1/(y-y_e)$ are plotted *versus* y, in Fig. 179. By trial and error it is found that an area of 3.3 is obtained when x_1 is taken as 1.63. The new conditions are now fulfilled, and it is found that the same tower will give the desired quality and quantity of gas when $x_1 = 1.63$. The slope of the operating line gives pounds H_2SO_4 per pound of dry air.

Present Conditions.

$$\text{Slope} = \frac{0.0093 - 0.0026}{1.145 - 0.101} = 0.00642.$$

Per 100 lb. of dry entering air, the weight of 90.8 per cent entering acid = 100(0.00642)/0.908 = 0.707 lb.

New Conditions.

$$\text{Slope} = \frac{0.020 - 0.0026}{1.63 - 0.101} = 0.0114.$$

Per 100 lb. of bone dry air, the weight of 90.8 per cent entering acid = 100 (0.0114/0.908 = 1.25 lb. The concentration of the effluent acid for the new conditions will be 100(1)/(1.63+1) = 38.0 per cent H_2SO_4, as compared with 46.6 per cent H_2SO_4 under present conditions.

Summary

	Present conditions	New conditions
y_1	0.0093	0.0200
y_0	0.0026	0.0026
x_0	0.1013	0.1013
x_1	1.145	1.63
$K_G a A l/G$	3.3	3.3
Pounds entering 90.8 per cent H_2SO_4 per 100 pounds dry air	0.707	1.25
Pounds water removed per 100 lb. dry air	0.670	1.74
Per cent H_2SO_4 in effluent acid	46.6	38.0

One finds that the present tower can be made to handle the saturated air, requiring the absorption of over twice the water removed at present, by increasing the entering acid from 0.71 to 1.25 lb. of 90.8 per cent H_2SO_4 per 100 lb. of bone-dry air. As a result the effluent acid will contain only 38 per cent H_2SO_4 instead of 46.6.

Note.—If the tower of Illustration 2 had been smaller, so that the effluent air, under both present and new conditions, had contained 6.11 g. of moisture per cubic meter of bone-dry air, calculation shows that the effluent acid would have to contain 50 per cent H_2SO_4 under the new conditions, as contrasted with an effluent acid containing 38 per cent H_2SO_4 for the new conditions of Illustration 2. In other words, in problems of this sort one cannot predict in advance whether the effluent acid under the new conditions will be stronger or weaker than under the old conditions. For the conditions outlined above calculation shows that the tower will be 49 per cent as tall as the tower of Illustration 2.

General Case.—In those important cases in which both gas and liquid film resistances must be taken into account, the graphical method of computation is of especial value. It is clear from Equation 2, p. 680, (see also p. 658) that $k_L/k_G = (y-y_e)/(x_e-x)$. Granting now that the ratio of the liquid and gas-film coefficients is known, by drawing through point P a line PD (Fig. 180), the slope of which equals k_L/k_G, it will be clear that the intersection D of this line with the equilibrium curve $OABC$ is the only point on the equilibrium curve which can possibly fulfil

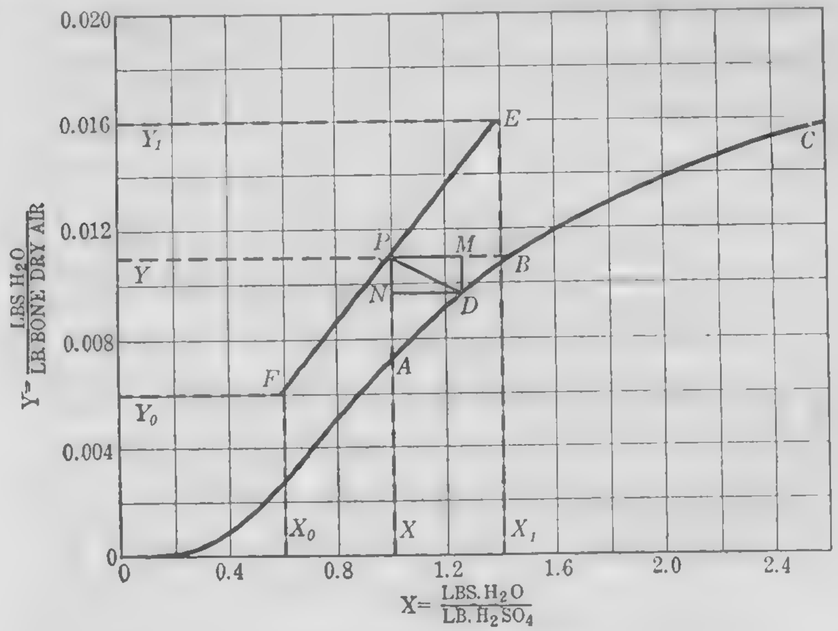


FIG. 180.—General Case.

this last relationship. It, therefore, follows that for such a case the concentration gradient through the gas film $y-y_e$ is equal to the line DM or PN, and that the gradient through the liquid film x_e-x is equal to the line DN or PM. In such a case the area curve is obtained by using these lines instead of one of the lines PA or PB, as before. From inspection it is obvious that PN is always less than PA, and PM less than PB; *i.e.*, the areas under the reciprocal curves are always greater. In other words, the rate of transfer through two films in series is less than if one film alone were present.

The preceding discussion has been based on the assumption that the driving forces or differences in potential ΔP and ΔC

are proportional to the concentration gradients Δy and Δx. It can readily be shown that, where concentrations are low, this is substantially true, but where concentrations are high, it is not true. In the latter case the diagrams of Figs. 174 to 180 should be constructed, not in terms of y and x, but in terms of partial pressures and concentrations P and C, or of whatever units of concentration must be chosen such that differences in concentrations expressed in these units are proportional to diffusion rates. On this diagram of P *versus* C the equilibrium curve should be

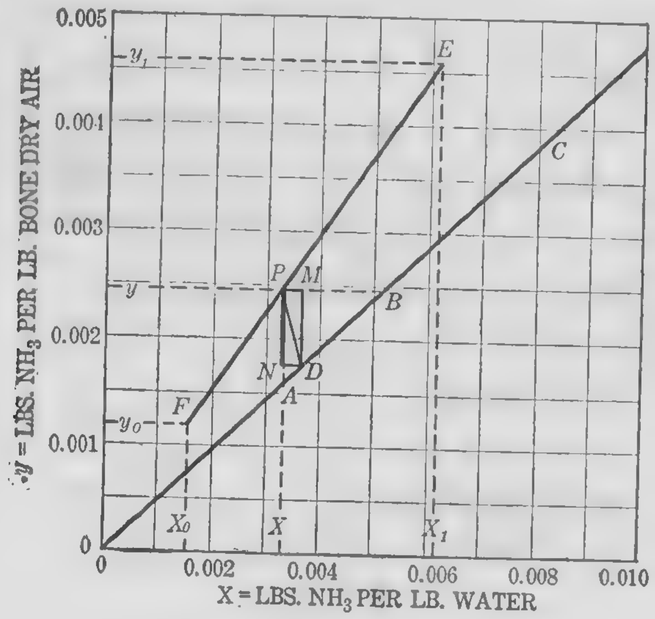


FIG. 181.—Henry's Law.

drawn. The actual curve, corresponding to the line FE, can be drawn by computation most conveniently by constructing first an auxiliary $x-y$ diagram and transferring the corresponding points from this diagram to the $P-C$ plane. The FE line will not be straight in the $P-C$ plane.

Henry's Law.—Figure 181 is a diagram similar to the two preceding ones for the case in which the concentration in the liquid phase is directly proportional to that in the gaseous phase, *i.e.*, $y=\alpha x$. Study of this diagram will show that, whatever the ratio of liquid-film to gas-film coefficient k_L/k_G, provided only that this ratio remains constant throughout the apparatus, at any particular point in the apparatus the actual driving force through the gas film PN divided by the vertical line PA, *i.e.*,

the driving force on the assumption that the resistance is entirely in the gas film, is numerically identical with this ratio at any other point. Since this ratio is constant throughout the apparatus, it therefore follows that the assumption of gas-film resistance only or, what is the equivalent to the same thing, the use of the line PA as the driving force will give a computed driving force proportional to the true one. In other words, it is allowable to assume a single film resistance for such a case; for, while the coefficient thus computed will differ from the true one, it will be constant and can be employed without hesitation. Similar analysis will show that it is equally allowable to assume the liquid film as controlling, for analogous reasons. In consequence, in those cases where Henry's law applies, it is usual and entirely allowable to assume either gas-film or liquid-film resistance only, neglecting the other one. It must, however, be kept in mind that the coefficients thus computed are not true gas-film or liquid-film coefficients, but are overall in character. Furthermore, their numerical values will vary with any changes in operating conditions which modify either the absolute or the relative resistances of the two films.

Further study of Fig. 181 (see p. 690) will make it clear that in this case the average driving force is the logarithmic mean of the driving forces at the beginning and end of the system, but that this simplification can be used only where Henry's law applies.[1] The possibility of using the logarithmic mean makes it easier to compute the performance of such a system algebraically than by the use of the graphical method outlined above, the formulas to be employed being as follows:

$$G(y_1-y_0)=\frac{dW}{d\theta}=k_G a A l(\Delta y)_{av} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $(\Delta y)_{av}$ is the logarithmic mean of the overall driving forces at the top and bottom of the tower.

$$L(x_1-x_0)=\frac{dW}{d\theta}=K_L a A l(\Delta x)_{av} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

[1] Unfortunately in the past the limitations on the applicability of the logarithmic mean for computation of absorption processes have not always been appreciated. One must not yield to the temptation of employing either of these simple forms of the general case where its applicability is open to question. Occasionally, however, the use of the logarithmic mean is allowable even though Henry's law does not apply, as for example, in the case of gases sufficiently soluble so that throughout the range involved the back pressure over the solution is negligible and gas film is controlling.

where $(\Delta x)_{av}$ is the logarithmic mean of the overall driving forces at the top and bottom of the tower.

In Eqs. (4) and (5), for low concentrations the values of Δx and Δy may be expressed in the stoichiometric units defined on page 676; for higher concentrations, Δy must in general be expressed in terms of pressure difference ΔP, and Δx as concentration difference ΔC (see p. 689). For very high concentrations the graphical methods must be used in terms of ΔP and ΔC.

Illustration 3.—In a continuous light-oil recovery plant, light oil is absorbed from coke-oven gas by solution in mineral oil, in a counter-flow absorption tower. The mineral oil enters the top of the tower with a negligible concentration of light oil, and the rich oil leaves the bottom with 2 lb. of benzene per 100 lb. of mineral oil. The gas treated contains 1.2 per cent by volume of benzene, toluene, xylenes, and similar hydrocarbons. The absorber recovers 86 per cent of the benzene in the entering gas and operates at 20° C. and at substantially normal barometric pressure.

What percentage recovery of the toluene, xylenes, and other hydrocarbons may be expected in this tower, neglecting the influence of the presence of the other components also absorbed, upon the vapor pressure of the benzene absorbed by the mineral oil?

Data.—The light oil in the entering gas contains 67 mol per cent of benzene, 12 per cent of toluene, and 7.1 per cent of xylenes. The remaining hydrocarbons, while constituting a very complex mixture, have an average boiling point of approximately 136° C. and an average molecular weight of 110. The light-oil solution at 20° C. follow Raoult's law when the average molecular weight of the oil is taken as 220. The gas-film resistance may be assumed to be of controlling importance.

Vapor pressure at 20° C.	Benzene	Toluene	Xylenes	Remaining hydrocarbons
Millimeters of mercury.....	75	22	5.2	5.4
Average molecular weight.....	78	92	106	110

Solution.—Assuming that the friction drop through the tower is such that the partial pressure of the coke-oven gas is substantially constant, one can compute the light oil absorbed from the decrease in light-oil pressure. Even if friction were negligible, thus causing the pressure of the coke-oven gas to increase somewhat, this assumption would introduce little error in this case, since the original percentage of light oil in the coal gas is so small.

First, the value of Ka_GV will be determined from the data regarding the *benzene* absorbed. Equation (4) (p. 691) is as follows;

$$\frac{W}{\theta} = K_G a V (\Delta y)_{av}$$

This equation will be used with the driving force Δy expressed as a pressure difference $(\Delta p)_{av}$. Let P represent the partial pressure of benzene in the gas and p the pressure of benzene in equilibrium with the wash oil, both in millimeters of mercury. As usual, the subscripts 0 and 1 refer to the top and bottom of the tower, respectively.

$$K_G a = \frac{\text{Mols absorbed}}{\text{(Unit time) (Unit volume of tower) (Atmospheric driving force, expressed in atmospheres)}}$$

G = Total mols of coke-oven gas per unit time.

$\frac{W}{\theta}$ = Mols absorbed per unit time $= G(P_1 - P_0)/760$.

V = Volume of tower $= Al$.

$(\Delta p)_{av}$ = Average driving force, in millimeters of mercury.

The light-oil pressure in the entering gas is 760 (0.012) = 9.12 mm.

$$P_1 = 9.12(0.67) = 6.11 \text{ mm.}; \quad P_0 = 6.11 \ (0.14) = 0.856 \text{ mm.}$$

Basis = 100 lb. of absorbent oil, free from light oil.

2/78 = 0.0257 mols benzene absorbed.

100/220 = 0.054 mols oil.

Neglecting the presence of the hydrocarbons absorbed, other than benzene, the total mols of liquid leaving are 0.48 (see note at end of solution). Mol fraction of benzene in solution at exit $= 0.0257/(0.0257 + 0.454) = 0.0535 = x_1$.

By Raoult's law, $p_1 = 75(0.0534) = 4.01$ mm.

Since the mol fraction of benzene in the entering wash oil $= 0 = x_0$; $p_0 = 0$.

Then $(\Delta p)_1 = 6.11 - 4.01 = 2.10$, $(\Delta p)_0 = 0.856 - 0 = 0.856$.

$$(\Delta p)_{av} = \frac{2.10 - 0.86}{2.3 \log \left\{ \frac{2.10}{0.856} \right\}} = 1.39 \text{ mm.}$$

$$\frac{W}{\theta} = G\left(\frac{P_1 - P_0}{760}\right) = \frac{K_G a V (\Delta p)_{av}}{760}$$

Whence

$$\frac{P_1 - P_0}{(\Delta p)_{av}} = \frac{K_G a V}{G} = \frac{6.11 - 0.86}{1.39} = 3.78 \text{ for benzene.}$$

Derivation of Equation for Recovery of Any Particular Component of the Light-oil Vapor.

m = Mol fraction of component in entering light-oil gas.

z = Fraction of this component remaining unabsorbed when gas leaves scrubber.

T = Vapor pressure of this component at 20° C., in millimeters of mercury.

Then $P_1 = 9.12m$: $P_0 = 9.12mz$: $P_1 - P_0 = 9.12m(1-z)$

Basis = 100 lb. of wash oil or 0.454 lb. mols.

Mols benzene absorbed = 0.0257.

Mols benzene in entering gas = 0.0257/0.86 = 0.0299.

Mols component in entering gas = $0.0299m/0.67 = 0.0446m$.

Mols component absorbed = $0.0446m(1-z)$.

$p_1 = T(0.0446)m\ (1-z)/0.480 = 0.0929m(1-z)\ T$.

$(\Delta p)_1 = P_1 - p_1 = m[9.12 - 0.0929T(1-z)]$.

$p_0 = 0$; $\Delta p_0 = P_0 - 0 = m9.12z$.

$$\frac{P_1 - P_0}{(\Delta p)_{av}} = \frac{m(9.12)\ (1-z)\ (2.3) \log \left[\frac{m9.12 - 0.0929T\ (1-z)}{m(9.12z)} \right]}{m[9.12 - 0.0929T\ (1-z) - 0.12z]} = \frac{K_G a V}{G} \quad (a)$$

But

$$(P_1-P_0)/(\Delta p)_{av}=K_Gav/G.$$

and the only term in the right-hand side of this equation, which changes with the component itself, is K_Ga. But as shown on page 661, for these units K_Ga varies inversely as the square root of M, the molecular weight of the gas absorbed. Since $K_Gav/G=3.78$ for benzene, where $M=78$, for any component,

$$K_Gav/G=3.78\sqrt{78}/\sqrt{M}=33.4\sqrt{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Eliminating K_Gav/G from Eqs. (a) and (b) one obtains

$$\frac{14.5-0.148T}{\sqrt{M}}=\log\frac{1-0.0102T\ (1-z)}{z} \quad . \quad . \quad . \quad . \quad (c)$$

Since the mol fraction m, of the component in the entering gas drops out of the equation, it is seen that the fraction of the given component absorbed depends only upon its molecular weight M and vapor pressure T. Substituting the proper values for M and T in Eq. (c), one obtains the following results;

For the toluene:

$M=92$, $T=22$, whence $z=0.053$.

For the xylenes:

$M=106$, $T=5.2$, whence $z=0.044$.

For the remaining hydrocarbons:

$M=110$, $T=5.4$, whence $z=0.047$.

The following table summarizes the results:

Component	Per Cent Recovery
Benzene	86.0
Toluene	94.7
Xylenes	95.6
Remaining hydrocarbons	95.3

Note.—To investigate the error in basing x only upon the mols of oil and benzene, rather than upon total mols, one must calculate the mols of toluene, xylene, and remaining hydrocarbons dissolved. Assuming 95 per cent recovery for all except benzene, the additional mols $=0.0446m(1-z)$. Taking m as 0.35 and $1-z$ as 0.95, one obtains 0.014 mol. Hence, the revised value of x for benzene would be $0.0257/(0.480+0.014)=0.0520$ *versus* 0.0535, or an error of 3 per cent, which would make little difference in the answers.

Illustration 4.—It is proposed to recover 6,000 lb. per 24 hr. of SO_2 from smelter gas containing 3.5 per cent SO_2 by volume, by scrubbing the gases with water in a counter-current absorption tower packed with 1-in. coke. There are available 1,500,000 cu. ft. per 24 hr. of a smelter gas saturated with water vapor at 68° F. and at normal barometric pressure. The effluent liquor is then to be rectified under pressure and the SO_2 vapor condensed to give liquid SO_2.

On the basis of the data and assumptions given below, calculate the diameter and height of the absorption tower required.

Data and Assumptions.—It is agreed that in no case should the superficial gas velocity exceed 1 ft. per second, and the liquor rate is not to exceed 50 lb. per minute per square foot of ground area. The molecular weight of the dry inert gas may be taken as 28.7. At 68° F., the vapor pressure of water is 17.5 mm. of mercury. Capacity coefficients for this case have been determined, see Fig. 191 (p. 713). For the sake of illustration, assume that the water used is 25 per cent in excess of the minimum amount corresponding to equilibrium between gas and liquor at the bottom of the tower. The appended table shows the equilibrium data for SO_2 and water at 68° F.

Equilibrium Solubility[1] of SO_2 in Water at 68° F.

Lb. SO_2/1000 lb. of water	1.0	2.0	3.0	5.0	7.0
SO_2 pressure, millimeters of mercury	3.2	8.5	14.1	26.0	39.0

[1] T. K. Sherwood, *Ind. Eng. Chem.*, **17**, No. 7 (July 1925), 745.

Solution to Illustration 4. *Cross-sectional Area of Tower.*—If the superficial gas velocity be taken as 1 ft. per second, the value of A would be (1,500,000)/(24) (3,600) (1) = 17.3 sq. ft. of total cross section.

The partial pressure of SO_2 in the entering gas is 0.035(760) = 26.6 mm. of mercury. From the table given, interpolation shows that the liquid in equilibrium with such gas contains 0.00509 lb. of SO_2 per pound of water. Since the weight of SO_2 to be absorbed is 6000/(24) = 4.17 lb., per minute the *minimum* water required will be 4.17/0.00509 = 820 lb. per minute. Since it is agreed to use 25 per cent excess water, the actual water used will be 820(1.25) = 1,025 lb. per minute. If the maximum allowable liquor velocity of 50 lb. per minute per square foot be used, the ground area of the tower will be (1,025+4.17)/50 = 20.5 sq. ft. Hence, in this case the cross-section is determined by the maximum allowable water rate. The corresponding diameter of the tower will equal $\sqrt{20.5/0.785}=5.16$ ft., or 5 ft. 2 in. The actual gas velocity will be 1,500,000/(24) (2,600) (20.5) = 0.848 ft. per second.

1. *Height of Tower, Based on the Logarithmic Mean* Δx.—The size of the tower will first be calculated based on the logarithmic mean driving force $(\Delta x)_{av}$. The actual weight ratio of SO_2 to water in the effluent liquor x_1 will be 4.17/1,025 = 0.00407. From the table of equilibrium data one finds that the value of x_e, in equilibrium with the SO_2 pressure of 26.6 mm., is 0.00509 lb. SO_2 per pound of water. The value of the driving force at the bottom of the tower $(\Delta x)_1=0.00509-0.00407=0.00102$.

To calculate the SO_2 pressure in the gas at the top of the tower, a material balance is used; basis = 1 min.

$$\frac{1{,}500{,}000\ (492)}{21\ (60)\ (528)\ (359)}=2.70 \text{ mols entering gases.}$$

2.70 (0.035) = ... 0.0947 mol SO_2 entering.
4.17/64 = ... 0.0652 mol SO_2 absorbed.

By difference ..... 0.0295 mol SO_2 in exit gas.

The tower would therefore recover 100(0.0652/0.0947) = 68.8 per cent of the SO_2 in the entering gas.

Water vapor condensed per minute $=0.0652(17.5/742.5)=0.00153$ lb. mol. Since the water vapor in the entering gas is $2.70(17.5/742.5)=0.0637$ mol per minute, the water vapor in the exit gas is $0.0637-0.0015=0.0622$ mol per minute.

	Mols per minute		
	In entering gas	In exit gas	Removed
SO_2 gas	0.0947	0.0295	0.0652
H_2O vapor	0.0637	0.0622	0.0015
Inert gas	2.54	2.54	none
Total mols	2.70	2.63	0.07

Hence, $\dfrac{0.0295\ (760)}{2.63}=8.53$ mm. SO_2 in exit gas.

By interpolation from the table of equilibrium data, the value of x_e at the top, corresponding to 8.53 mm., is 0.00201 lb. SO_2 per pound of water. Since fresh water enters at the top, $x_0=$ zero, and $(\Delta x)_0=0.00201-0=0.00201$. Using the logarithmic mean value of Δx,

$$(\Delta x)_{av}=\frac{0.00201-0.00102}{2.3\log\dfrac{0.00201}{0.00102}}=0.00146.$$

The value of $1/Ka_G$ from Fig. 191 is determined by the value of $1/g^{0.8}$. The value of g varies only slightly at different points in the tower; hence the smallest value of g, that at the top, will be taken.

Pounds $SO_2=0.0295(64)=$	1.9
Pounds dry inert gas $=(2.54)(28.7)=$	72.9
Pounds H_2O vapor $=(0.0622)(18)=$	1.1
Pounds exit gas per minute	75.9

Mass velocity $=\dfrac{75.9}{20.5}=3.70$ lb. per minute per square foot $=g$.

$\dfrac{1}{g^{0.8}\sqrt[3]{(L/A)}}=\dfrac{1}{3.9^{0.8}\sqrt[3]{50}}=0.0954$. From Fig. 191, the corresponding value of $1/Ka_G=338$, and hence

$$Ka_G=0.00296\frac{\text{lb. } SO_2}{(\text{minute})\ (\text{cubic foot tower})\ (\text{millimeter of mercury } \Delta p)}.$$

The above value of Ka_G was determined from data at 56° F., whereas this tower is to operate at 68° F. While ka_L, and hence Ka_G, would increase somewhat from 56 to 68° F., such change will be ignored, thereby introducing a small factor of safety in the design.

To convert from K_Ga to K_La, one remembers that $K_La=K_Ga/H$, see p. 658. Since the Henry's law coefficient H varies with x, H will be determined for an average value of x of 0.002, where the equilibrium SO_2

pressure is 8.5 mm.; whence $H=0.002/8.5=0.000235$. Hence $K_La=0.00296/0.000235=12.6$.

Since the SO_2 absorbed is 4.17 lb. per minute, and $\Delta x_{av}=0.00146$,

$$\frac{4.17}{(12.6)\ (0.00146)}=227 \text{ cu. ft. of tower required.}$$

Since the ground area is 20.5 sq. ft., the height of l of packing equals $227/20.5=11$ feet.

2. *Height of Tower Based on Logarithmic Mean Δp.*—If the same problem be solved, based on the overall coefficient on the gas-film basis, one finds the following values:

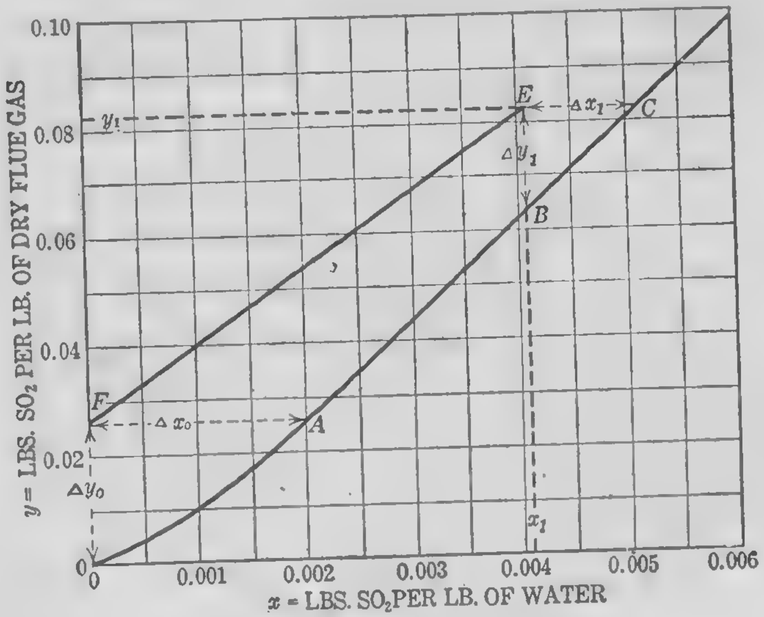


FIG. 182.—Diagram for Problem 4.

$(\Delta p)_1=26.6-20.5=6.1$; $(\Delta p)_0=8.53-0=8.53$.

$(\Delta P)_{av}=7.29$ mm.; $K_Ga=0.00296$.

$$V=\frac{4.17}{(7.29)\ (0.00296)}=193=Al, \text{ and } l=193/20.5=9.4 \text{ ft.}$$

The discrepancy between the values of l, 11 and 9.4, is due to the fact that Henry's law does not hold, and hence the logarithmic mean driving force is incorrect.

3. *Height of Tower Calculated from a Graphical Integration, Based on K_La.*—It now becomes necessary to plot the equilibrium curve in stoichiometric units y *versus* x. For example, when $x=0.002$ lb. SO_2 per pound of water, $p=8.5$ mm., and the corresponding value of $y=(8.5)(64)/(760-8.5-17.5)(28.7)=0.0258$ lb. SO_2 per pound of inert. Repeating for other values of x, the corresponding values of y are plotted *versus* x, giving the equilibrium curve $OABC$ of Fig. 182.

The coordinates of the ends of the operating line are as follows:

$$y_1 = \frac{(26.6)\ (64)}{(760-26.6-17.5)\ (28.7)} = 0.0829;\ x_1 = 0.00407.$$

$$y_0 = \frac{(8.53)(64)}{(760-8.53-17.5)\ (28.7)} = 0.0259;\ x_0 = \text{zero}.$$

These values are plotted on Fig. 182, and are connected by the line *FE*, giving the operating line. The *horizontal* distances between *FE* and *OABC* represent the numerical values of the driving force $x_e - x$. The area under the curve of $1/(x_e - x)$ *versus* x, between the limits of $x_1 = 0.00407$ and $x = 0$ gives 2.75.

$$\text{But} \int_{x_0=0}^{x_1=0.00407} \frac{dx}{x_e - x} = K_L a A l / L.$$

Or $2.75 = (12.6)(20.5)(l)/1{,}025$, whence $l = 10.9$ ft.

4. *Calculation of Height from Graphical Integration, Based on $K_G a$.*—The values of $y - y_e$ are determined by the *vertical* distances between the operating line *FE* and the equilibrium curve *OABC* of Fig. 182. Upon plotting the reciprocal of $1/(y - y_e)$ *versus* y, the area between $y_1 = 0.0829$ and $y = 0.0259$ is found to be $2.23 = K_G a\ Al/G = 0.00296(20.5)l/72.9$, whence $l = 8.2$ ft.

Summary.

	Height of Tower, Expressed in Feet
1. $K_L a$ and logarithmic mean Δx	11.0
2. $K_L a$ and graphical integration, $dx/(x_e - x)$	10.9
3. $K_G a$ and logarithmic mean Δy	9.4
4. $K_G a$ and graphical integration, $dy/(y - y_e)$	8.2

One, therefore, concludes that the height calculated from the logarithmic mean Δx is safe in cases of this kind, *i.e.*, where the equilibrium curve of y *versus* x is *concave upwards*, see Fig. 182. In this case the factor of safety introduced by using the logarithmic mean is only 1 per cent of the value calculated from the graphical integration of $dx/(x_e - x)$. This deviation is small because the equilibrium relation between y and x is almost linear over the range involved, *i.e.*, from *A* to *C*.

The height calculated from the logarithmic mean Δy is 15 per cent greater than that based on the graphical integration of $dy/(y - y_e)$, the increased deviation being due to the fact that the equilibrium relation has considerable curvature over the range involved, from *O* to *B*.

Of the two heights calculated from the graphical integrations, that based on $K_L a$ is the more reliable, as under these operating conditions the liquor-film resistance[1] is the major fraction of the total resistance, 212/338 or 62.7 per cent.

To offset the lack of absolute reproducibility of the overall coefficients, and to allow for uncertainties in operating conditions, a factor of safety of roughly 50 per cent is recommended; hence the tower should be 10.9(1.5) ft. tall, say 16 ft.

[1] As shown by Fig. 191, the intercept is 212, *versus* $1/K_G a = 338$.

Notes on Operation of Scrubbers

Complex Mixtures.—The preceding discussion has been limited to the assumption that one is absorbing only a single component from the gas. Frequently, however, a number of components are dissolved. Sometimes it is desirable to dissolve a whole group of compounds, *e.g.*, in the recovery of light oil from coke-oven gas, one wishes to secure not only the benzene but also toluene, xylene and other high boiling hydrocarbons, as discussed in the illustration on p. 692. In other cases, the solution of certain components is undesirable, but unavoidable because of their solubility, as in the solution of hydrogen sulphide and carbon dioxide in the ammonia liquor obtained by scrubbing ammonia out of coal gas.

Where it is desired to recover a number of components, one should design so as to recover the least soluble of these. The others will then be recovered even more completely than the first, provided they are not present in preponderating amounts. In the latter case the absorption system must be designed for the one most difficult to dissolve in view of both its solubility and its quantity. Where the very soluble components are present in considerable quantity, by their influence upon the equilibrium relationships, they sometimes considerably affect the solubility of the less soluble ones in the absorbing menstrum, and in such cases due allowance must be made therefor.

Ratio of Liquid to Gas.—Consider a counter-current gas washing system in which not only the component desired is soluble in the absorbent but also some other component of the gas is at least somewhat so. Both these components will dissolve, but the second less than the first. If one employ an absorption column sufficiently long and efficient, one can saturate the absorbent with the desirable component at the point where the absorbent leaves the column, but it is impossible completely to dissolve the desired component with a smaller amount of absorbent than this; in general one will have to use more absorbent, the excess quantity depending upon the size and efficiency of the tower. Even this minimum amount of absorbent will, however, dissolve some of the undesirable constituents and, furthermore, the greater the quantity of excess absorbent, the more of the undesirable constituents will go into solution. Since, however, excess absorbent cannot possibly dissolve more of the desired

constituent, because the theoretical quantity, *properly used*, will dissolve it all, excess absorbent merely increases the ratio of undesirable to desirable material. One, therefore, obtains the following rule:

If the gas being treated in a counter-current absorption system contains a component which it is not desired to dissolve but which is appreciably soluble in the solvent employed, one should use an absorption column designed to give the most efficient possible counter-current contact between absorbent and gas and strictly limit the amount of absorbent used per unit of gas treated to the lowest possible quantity adequate to dissolve the desired constituents.

Unfortunately, the gas treated is often subject to variations both in composition and quantity. With regard to the composition, whenever the solubility of the constituent to be absorbed follows Henry's law, the minimum adequate ratio of absorbent to gas treated is independent of the composition. Thus, assume a certain composition and a corresponding ratio of absorbent to gas; if, now, one double the concentration of the desired constituent in the entering gas, since its solubility in the absorbing medium is proportional to its concentration, the absorbing capacity of the menstrum is doubled. Therefore, there need be no increase in the quantity of the absorbing medium per unit quantity of gas treated in order to dissolve the increased amount of the solute. This can be summarized in the following rule:

For a given material to be dissolved from a gas in a given absorbing liquid in which the solubility of the material follows Henry's law, the minimum adequate quantity of absorbent per unit quantity of gas treated is independent of the concentration of the material absorbed.

From the above it follows that, to get best results, the ratio of absorbent to gas treated should be kept constant.

Materials Obeying Raoult's Law

In the case of a volatile liquid dissolved in an essentially non-volatile solute, in the presence of a substantially insoluble gas, the partial pressure of the dissolved vapor following Raoult's law, the equilibrium relationships are greatly simplified. While the following discussion will be general, it will perhaps be clearer to illustrate by the case of benzene vapor dissolved from an inert

gas, such, for example, as flue gas, by absorbent oil, the oil being later denuded by distillation with steam. It is assumed that both the absorption and stripping are conducted by counter-current flow, under steady conditions of operation. Call x^1 the mols of benzene per mol of oil, in the liquid phase, and y the mols of benzene per mol of gas (flue gas or steam as the case may be). In the operation under consideration, L mols of absorbent oil and G mols of gas are employed per unit time. It is obvious from a material balance (see page 677) that the equation,

$$L(x_o - x) = G(y_o - y) \qquad (1)$$

represents the actual operating conditions in the unit. If now one assume constancy of temperature in the tower, calling P the pressure of pure benzene at this temperature and π the total pressure on the unit, the partial pressure of benzene over the

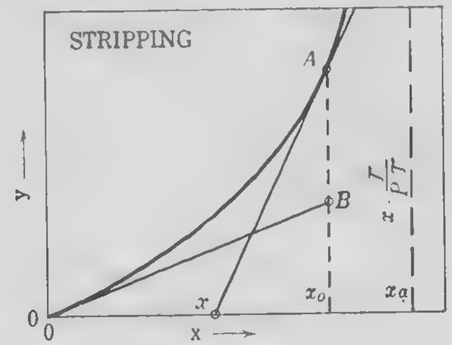


FIG. 183.

liquid p is given by the expression, $p = Px/(1+x)$, while the partial pressure of benzene in the gas is $p_g = \pi y/(1+y)$. At equilibrium these two are equal, *i.e.*,

$$y = \frac{Px}{\pi - (P-\pi)x} \qquad (2)$$

This equation represents a rectangular hyperbola with axes parallel to the major axis.

Special Cases: I: $P > \pi$.—When stripping a volatile component from a non-volatile absorbent by steam it is advantageous to have the temperature as high and the pressure as low as possible (see page 667). Generally, therefore, the operating conditions are such that $P > \pi$. In this case inspection of the equilibrium, Eq. (2), shows that y becomes infinite when the denominator on the right hand side is zero, *i.e.*, when $x_a = \pi/(P-\pi)$, where x_a is the asymptotic value above which the concentration

[1] These units differ from those employed on pages 675 to 698.

of the dissolved constituent in the absorbent liquid cannot exist. If the absorbent enters the stripping column richer than this, the excess of dissolved vapor boils out spontaneously, reducing the concentration to the asymptotic value. The equilibrium curve is represented by Fig. 183, p. 701.

If, in this figure, x_o represents the concentration of the incoming rich absorber stock, inspection will make it clear that, if one wishes to secure complete stripping, *i.e.*, to have the operating line go through the origin, the steepest line which can be drawn is one tangent to the equilibrium curve at the origin, cutting the vertical line through x_o at the point B, this point corresponding to the highest possible degree of saturation of the steam leaving the stripping column under these conditions.

Inspection of the equilibrium, Eq. (2), shows that its slope is given by the expression,

$$\frac{dy}{dx}=\frac{P\pi}{[\pi-(P-\pi)x]^2} \qquad (3)$$

Therefore, for complete stripping, the operating line has for its slope the value of this expression at $x=0$, *i.e.*, $dy/dx=P/\pi$ or $dx/dy=\pi/P=G/L$, where G/L is the mols of steam required per mol of oil. Furthermore, it is obvious in this case that the equation of the operating line is $y=(P/\pi)x$ and that the steam consumption is proportional to the total pressure on the system and inversely proportional to the pressure of the pure solute at the operating temperature. In other words, the lower the total pressure the less the steam consumption necessary for complete stripping, and also the lower the volatility of the absorbed component the greater the steam necessary to do the work. Inspection, both of the diagram and of these equations, shows that the steam consumption for complete stripping is independent of the initial concentration of the rich absorber stock. From this it follows that if one is stripping from the oil a mixture of a number of dissolved components, since the more volatile strip out first, the steam necessary for complete stripping is that computed for the least volatile component, just as though the others were not present.

If one wishes to saturate the steam leaving the stripper, *i.e.*, to bring it into equilibrium with the incoming rich stock, the steepest operating line attainable is a tangent to the equilibrium curve at point A, cutting the horizontal axis at point C, corresponding to the best possible stripping compatible with the assumption

made. The equation of this line can be calculated from its slope,

$$\frac{dx}{dy}=\frac{G}{L}=\frac{[\pi-(P-\pi)x_o]^2}{P\pi}, \text{ whence,}$$

$$x_o-x=\frac{[\pi-(P-\pi)x_o]^2\,(y_o-y)}{P\pi}.$$

Hence at the bottom of the apparatus, where $y=0$,

$$x=x_o-y_o\frac{[\pi-(P-\pi)x_o]^2}{P\pi}.$$

This value of x represents the lowest attainable concentration of the stripped oil compatible with steam saturation at the top.

If $x_o=x_a$, inspection of the diagram makes it clear that it is impossible to strip at all and at the same time have the vapors leaving the still at equilibrium with the absorber stock entering it. This is true because, under these conditions, the partial pressure of the entering absorber stock is equal to the total pressure on the still, so that the presence of any steam whatever would

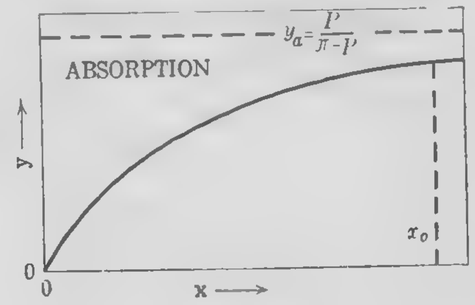


FIG. 184.

lessen the partial pressure of the solute and therefore destroy the equilibrium.

If, as is usually the case, a large fraction but not all of the benzene in the feed is to be removed, then x_1 is small but finite. The minimum steam consumption would then correspond to equilibrium at some value of x intermediate between x_o and x_1, the operating line being tangent to the equilibrium curve at $x_i=\sqrt{\frac{\pi x_1}{P-\pi}}$. Obviously this value of x is independent of x_o and depends only on x_1, π, and P. Since the values of y_i, x_i, and x_o are known, y_o is computed by proportion: $y_o=y_i(x_o-x_1)/(x_i-x_1)$.

Case II: $P<\pi$.—Absorption should take place at the highest practicable total pressure and the lowest possible temperature,

i.e., at high values of π and low of P. In other words, the conditions of this case ($P<\pi$) are those normally existing in absorption processes but not in stripping.

Inspection of the equilibrium equation makes it clear that it corresponds to the curve of Figure 184, being asymptotic to the horizontal line, $y=P/(\pi-P)$.

It is obvious that if one desires to completely denude the gas, the operating line must go through the origin and cannot possibly have a slope less than that corresponding to tangency there. Since at $x=0$, $dy/dx=P/\pi$, the corresponding operating line is $y=Px/\pi$ and the amount of absorbent required per mol of inert

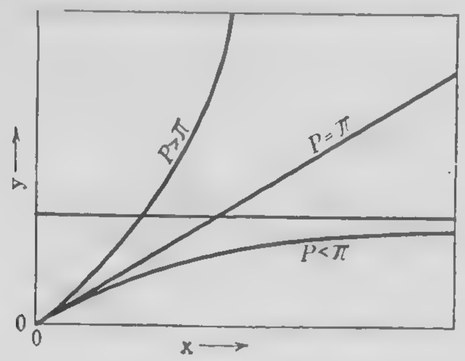


FIG. 185.

gas treated, $L/G=P/\pi$. It will be noted that the absorbent required for a given amount of gas is proportional to the volatility of the solute absorbed and inversely proportional to the total pressure of the system. Here, too, the absorbent needed is independent of the initial concentration in the other phase at the other end of the unit. Since $y=Px/\pi$, it is obvious that $x_o=\pi y_o/P=$ the maximum saturation of oil compatible with complete denuding of the gas treated.

To saturate oil up to equilibrium with the gas entering the absorber,

$$y_1=y_o-\frac{P\pi x_o}{[\pi+(\pi-P)x_o]^2}$$

This gives the lowest value to which the concentration of solute vapor in the exit gas can be reduced if the oil is brought up to equilibrium with the entering gas.

Case III: $P=\pi$.—For this case at equilibrium $y=x$ and it is therefore possible to have equilibrium at all points in the system,

provided the capacity of the equipment be sufficient to carry out the absorption under a negligible driving force.

The conditions for the three cases are given in Fig. 185, the upper curve corresponding to stripping, the lower to absorption, and the straight line between them to the special case of $P=\pi$. It is worth noting that, in both stripping and absorption, one normally operates on the unfavorable side of the equilibrium curve, *i.e.*, it is theoretically impossible to secure equilibrium at both ends of the operating line. Were one absorbing under conditions corresponding to the upper curve or stripping under those of the lower, the reverse would be true. However, this disadvantage is more apparent than real, because the height of the equilibrium curve corresponding to stripping conditions, secured by raising the temperature and lowering the pressure, far more than compensates for its unfavorable shape and the same is true of the advantages gained by lowering the equilibrium curve for absorption, through decreased temperature and increased pressure.

While for many cases of absorption Raoult's law does not apply,[1] there are important instances, notably the absorption of hydrocarbons in oil, where it is an entirely satisfactory approximation. Furthermore, even in those cases where the deviations from it are too wide to justify its quantitative use, it none the less gives a clear visualization of the qualitative effects of various factors upon operating results.

CAPACITY COEFFICIENTS FOR PROCESSES OF ABSORPTION AND DESORPTION

This section of the chapter is devoted to a discussion of the quantitative capacity coefficients for different types of apparatus, as affected by factors such as gas velocity, liquid velocity, temperature, nature of gas and liquid used, and the dimensions of the apparatus. As shown on page 658, the relationship between the *overall* coefficients K and the *individual* coefficients, k is given by the following equations:

$$\frac{1}{K_G}=\frac{1}{Hk_L}+\frac{1}{k_G}=\frac{1}{Hk_L}+\frac{1}{bg^{0.8}} \quad \ldots\ldots\ldots (6)$$

$$\frac{1}{K_L}=\frac{1}{k_L}+\frac{H}{k_G}=\frac{1}{k_L}+\frac{H}{bg^{0.8}} \quad \ldots\ldots\ldots (7)$$

[1] See p. 583.

$$K_G = HK_L \quad \ldots \quad (g)$$

$R_G = 1/K_G$; $R_L = 1/K_L$

Unless otherwise specified, data will be given in the following units.

TABLE

K_L and $k_L = \dfrac{\text{Lbs. absorbed}}{\text{(Min.) (sq. ft. interface) (unit driving force in lbs. per cu. ft.)}}$.

K_G and $k_G = \dfrac{\text{Lbs. absorbed}}{\text{(Min.) (sq. ft. interface) (unit driving force in mm. of mercury)}}$.

$\dfrac{L}{A}$ = Liquor velocity, in $\dfrac{\text{Pounds liquid}}{\text{(Minute) (square foot of ground area)}}$.

g = Gas velocity, in $\dfrac{\text{Pounds gas}}{\text{(Minute) (square foot of ground area)}}$.

l = Height of tower, in inches.
d = Diameter of tower, in inches.
b = Constant in the equation: $k_G = bg^{0.8}$.
M = Molecular weight of diffusing gas.

H = Henry's law constant in $\dfrac{\text{Pounds per cubic foot}}{\text{Millimeters of mercury}}$.

$$f = \frac{b}{\sqrt{M}} = \frac{k_G}{\sqrt{M}(g^{0.8})}; \quad B = \frac{f}{(d/l)d^{0.3}}.$$

Absorption of Gases in Wetted-wall Towers.—In a wetted-wall tower it seems reasonable to assume that the effect of changing the mass velocity of the gas has a negligible effect upon the resistance of the liquor film. Equations (6) and (7)(p. 705) indicate that in such cases one should plot overall absorption resistance against $1/g^{0.8}$. This method of interpreting the overall coefficients will be illustrated by showing data[1] for the absorption of SO_2 from air by water in a tower 3-in. in diameter and 36-in. high, first by plotting $1/K_L$ against $1/g^{0.8}$ (Fig. 186) and second, by plotting the same experimental data expressed as $1/K_G$ against $1/g^{0.8}$ (Fig. 187). Relationships calculated from these plots are given in Tables A and B.

[1] HASLAM, HERSHEY, and KEAN, *Ind. Eng. Chem.*, **16**, No. 12 (December, 1924).

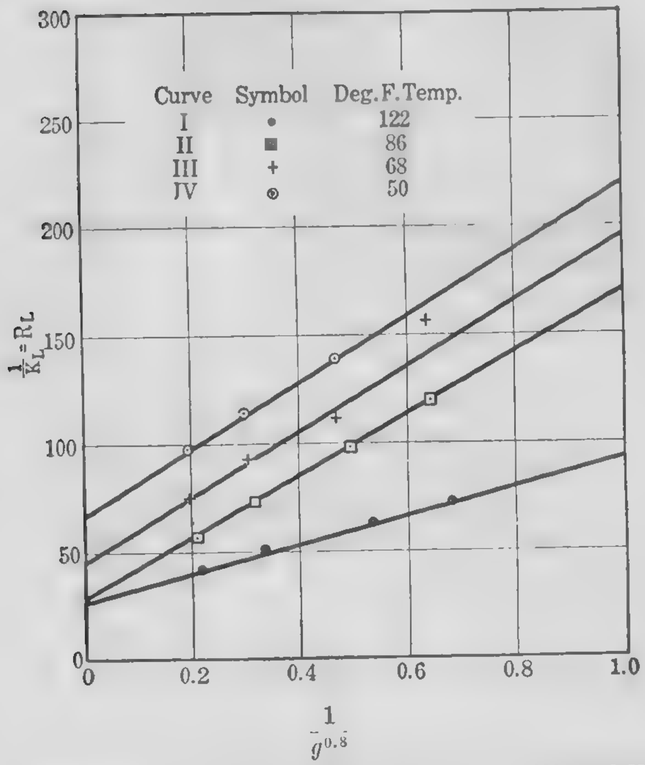


FIG. 186.—Absorption of SO_2 from Air by Water in a Wetted-Wall Tower

TABLE A, BASED ON FIG. 186

Curve	1 Temp. deg. F.	2 Intercept $1/k_L$	3 k_L	4 Viscosity z_L	5 $k_L z_L$	6 Slope H/b	7 Solubility H	8 $b \times 10^6$
IV	50	67	0.015	1.30	0.019	153	0.0272	178
III	68	46	0.022	1.00	0.022	149	0.0147	99
II	86	29	0.035	0.80	0.028	141	0.0106	75
I	122	27	0.037	0.55	0.020	66	0.0040	61

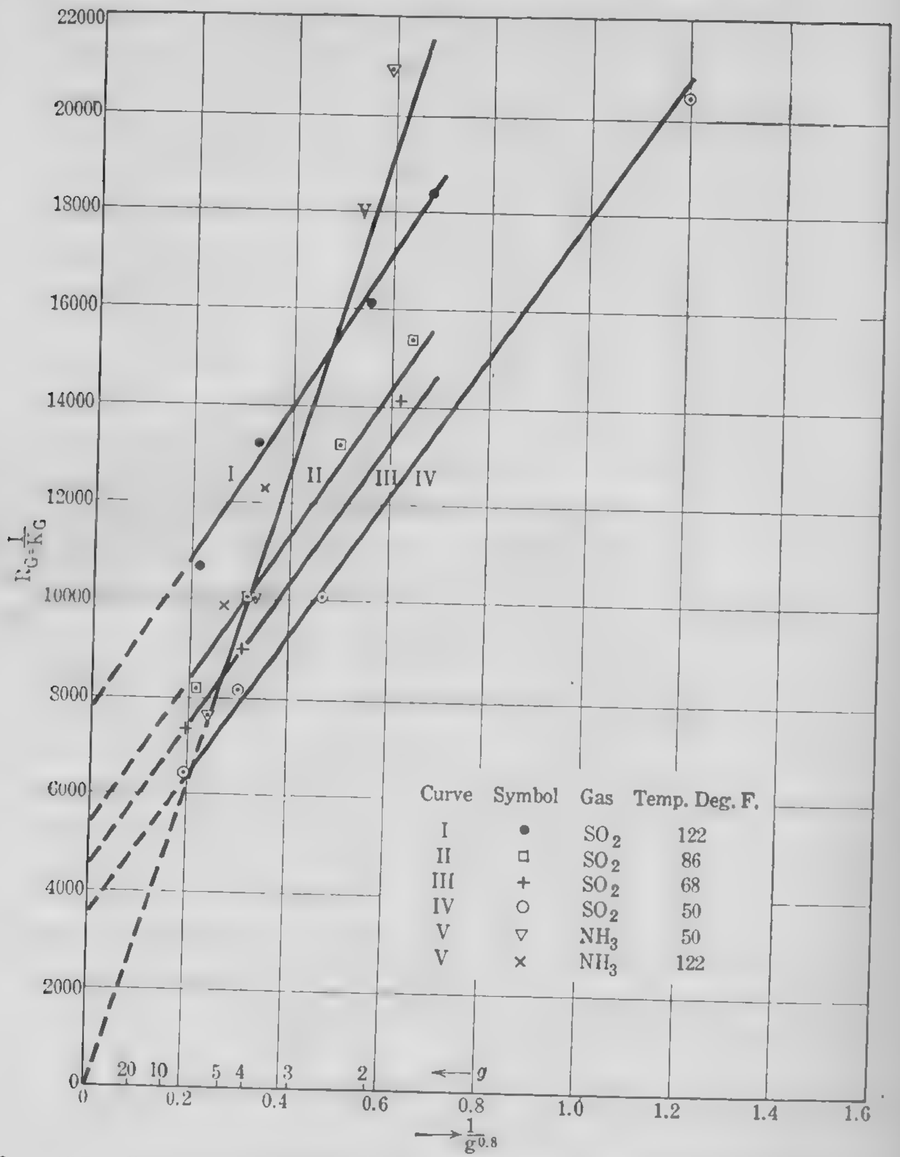


FIG. 187.—Separate Absorption of Gases from Air by Water in Wetted-Wall Towers.

TABLE B, BASED ON FIG. 187

Curve	1 Temp. deg. F.	2 Intercept $1/Hk_L$	3 Solubility H	4 k_L	5 z_L	6 $k_L z_L$	7 Slope $1/b$	8 $b \times 10^6$
IV	50	3,550	0.0272	0.0104	1.30	0.014	14,400	69.4
III	68	4,550	0.0147	0.0150	1.00	0.015	14,600	68.5
II	86	5,400	0.0106	0.0175	0.80	0.014	15,000	66.7
I	122	7,750	0.0010	0.0320	0.55	0.018	15,600	64.1

In both plots the intersections of the lines with the vertical axes represent individual values for $1/k_L$ and $1/Hk_L$ respectively. $1/k_L$ is highest at the lowest temperature, doubtless due to the fact that the viscosity z_L of the liquid is greatest at the lowest temperature, while $1/Hk_L$ is greatest at the highest temperature, although k_L falls in the same order, as may be seen from column 3 of Table A and column 4 of Table B.

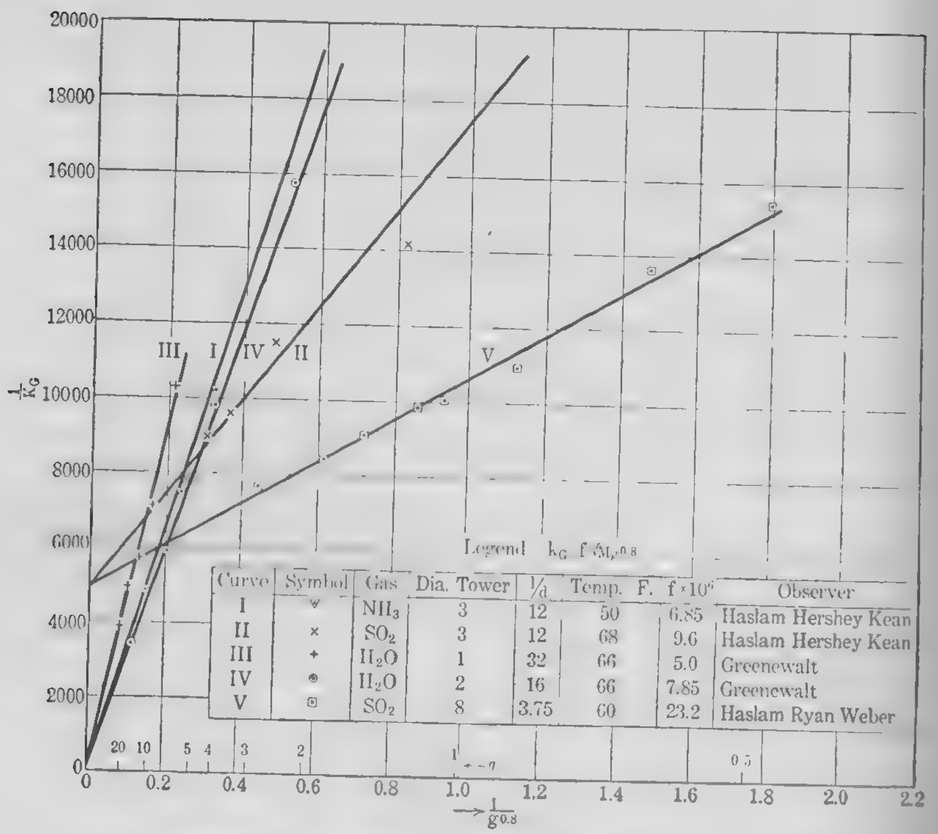
Based on a study of these plots one concludes that (1) k_L increases rapidly with increase in temperature and that the product of k_L and the viscosity z_L of the liquid is subtantially constant; (2) although somewhat misleading, b apparently depends upon temperature as shown in Table A, while from Table B, b is independent of temperature, as should be the case (see p. 660).

Due to the fact that H, even at a given temperature changes somewhat with concentration of SO_2 in the liquid, *i.e.*, Henry's law does not apply, the numerical values of b and k_L as determined by the two methods of expressing data do not agree. When the resistances of both films are important therefore, it is incorrect to apply an overall coefficient, as was pointed out on page 691.

On Fig. 187 are also plotted data for ammonia absorbed from air by water, at two different temperatures, and it is found that the liquor-film resistance is substantially zero, as shown by the negligible intercept of curve V on the vertical axis. In other words, the gas-film resistance is of controlling importance in the case of ammonia in water, while for sulphur dioxide in water both resistances must be taken into account. The values of b for ammonia, as determined from this plot, are independent of temperature, and due to the lower molecular weight, are numerically smaller than for SO_2, being 0.000031 and 0.000067 respectively. As shown on page 660, when using the units here employed, b should equal $f\sqrt{M}$. Hence, these data give $f=0.000031/\sqrt{17}=0.0000075$ for ammonia and $f=0.000067/\sqrt{64}=0.0000084$ for SO_2, giving a mean value of $f=8/10^6$.

Figure 188 is a plot similar to Fig. 187 and summarizes absorption data obtained at temperatures ranging from 50 to 68° F. in four sizes of wetted-wall towers by three different observers.[1] Curve I shows the results for the absorption of NH_3

[1] HASLAM, HERSHEY, and KEAN, *loc. cit.* GREENWALT, *Ind. Eng. Chem.*, **18** (1926), 1291. HASLAM, RYAN, and WEBER, *Trans. Am. Inst. of Chem. Eng.*, **15**, (1923), 177.



Curve	Symbol	Gas	Dia. Tower	l/d	Temp. F.	$f \times 10^6$	Observer
I	⊙	NH_3	3	12	50	6.85	Haslam Hershey Kean
II	×	SO_2	3	12	68	9.6	Haslam Hershey Kean
III	+	H_2O	1	32	66	5.0	Greenewalt
IV	⊛	H_2O	2	16	66	7.85	Greenewalt
V	⊡	SO_2	8	3.75	60	23.2	Haslam Ryan Weber

FIG. 188.—Separate Absorption of Various Gases from Air by Water in Wetted-Wall Towers.

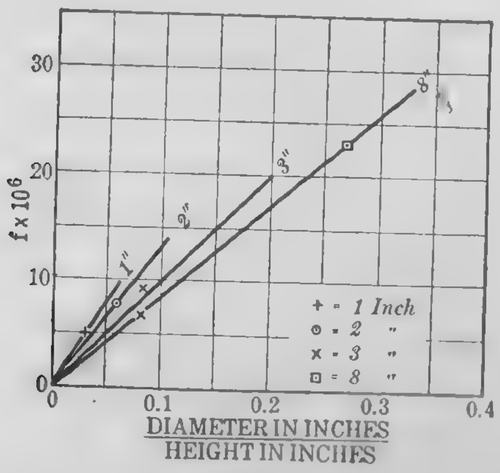


FIG. 189.

from air by water, while curves III and IV show the results when absorbing water vapor from air in sulphuric acid. In these three cases the intercepts or values of the liquor-film resistances are zero, indicating that the gas-film resistances are of controlling importance. Curves II and V show the results of absorbing SO_2 from air by water in two different sizes of towers, and it is seen that the liquor-film resistance is a considerable fraction of the total resistance. From the values of b as determined by Fig. 188, the corresponding values of f were obtained by dividing b by $\sqrt{M}$. On Fig. 188 are tabulated the values of $f \times 10^6$, and also the corresponding values of the ratio of height to diameter, when both l and d are expressed in the same units. Figure 189 shows $f \times 10^6$ plotted *versus* d/l, and the plot indicates that f increases with increase in d/l since for short towers the turbulence at entrance would be abnormally high. It is known that heat transfer at a given net velocity increases as the friction or degree of turbulence is increased, as in short pipes (see p. 140). It seems reasonable that the same principle would hold for absorption, since the capacity coefficients for both processes increase as film thickness is decreased (see p. 39). Were sufficient data available one would expect the points of Fig. 189 to fall on various curves, one for each diameter, the curve for the smallest diameter being the highest, as shown by the lines drawn on Fig. 189. For the sake of illustration assume that $f \times 10^6/(d/l) = B/d^n$. By determining the constants from the data on Fig. 189 one obtains $f \times 10^6 = 155(d/l)/d^{0.3}$, where d is expressed in inches. The following table shows the agreement between the observed and calculated values of $f \times 10^6$.

l/d, number of units	d, inches	$f \times 10^6$	
		Observed	Calculated
3.75	8	23.2	22.1
12.0	3	9.6	9.3
12.0	3	6.85	9.3
16.0	2	7.85	7.9
32.0	1	5.0	4.8

The agreement is better than would be expected when one remembers, first, that these data were obtained by different investigators, and second, that the data for SO_2 in water have been

expressed in terms of the overall coefficient K_G; yet the Henry's law coefficient H for SO_2 is not independent of concentration over the range used experimentally, see p. 709.

To correlate these data for the separate absorption of three different gases from air by water in wetted-wall towers, the value of K_G may be calculated as follows:

$$\frac{1}{K_G}=\frac{1}{k_G}+\frac{1}{Hk_L}.$$

$$k_G=\frac{155\sqrt{M}g^{0.8}}{10^6 d^{0.3}(l/d)}.$$

For ammonia or water vapor, $1/Hk_L=0$. For sulphur dioxide and carbon dioxide, $k_L=0.019/z_L$.

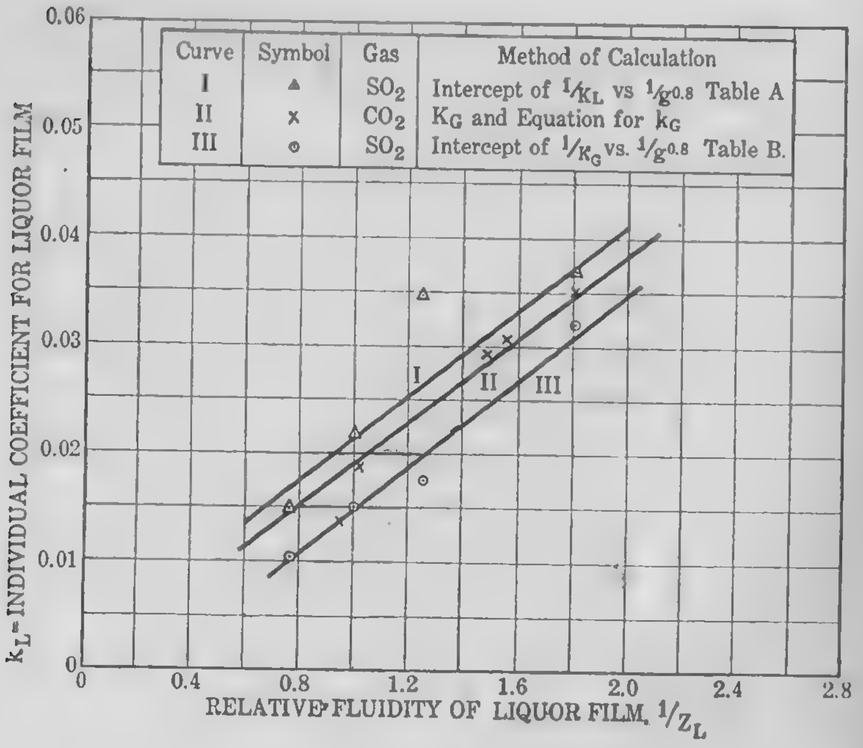


FIG. 190.

These equations are derived to illustrate the method of attack rather than to obtain a general equation for wetted-wall towers. Obviously they should be extrapolated with caution.

Figure 190 shows a plot of k_L *versus* the fluidity, $1/z_L$, as suggested by the relation $k_L z_L$ = constant. It is seen that the relation is approximately linear, and that the data for the

removal of CO_2 from air by water fall between the two curves for the absorption of SO_2 from air by water, based on Tables A and B, pp. 707 and 708.

Absorption of Gases in Packed Towers.—Figure 191 shows a plot of data[1] for the separate absorption of SO_2 and NH_3 from air

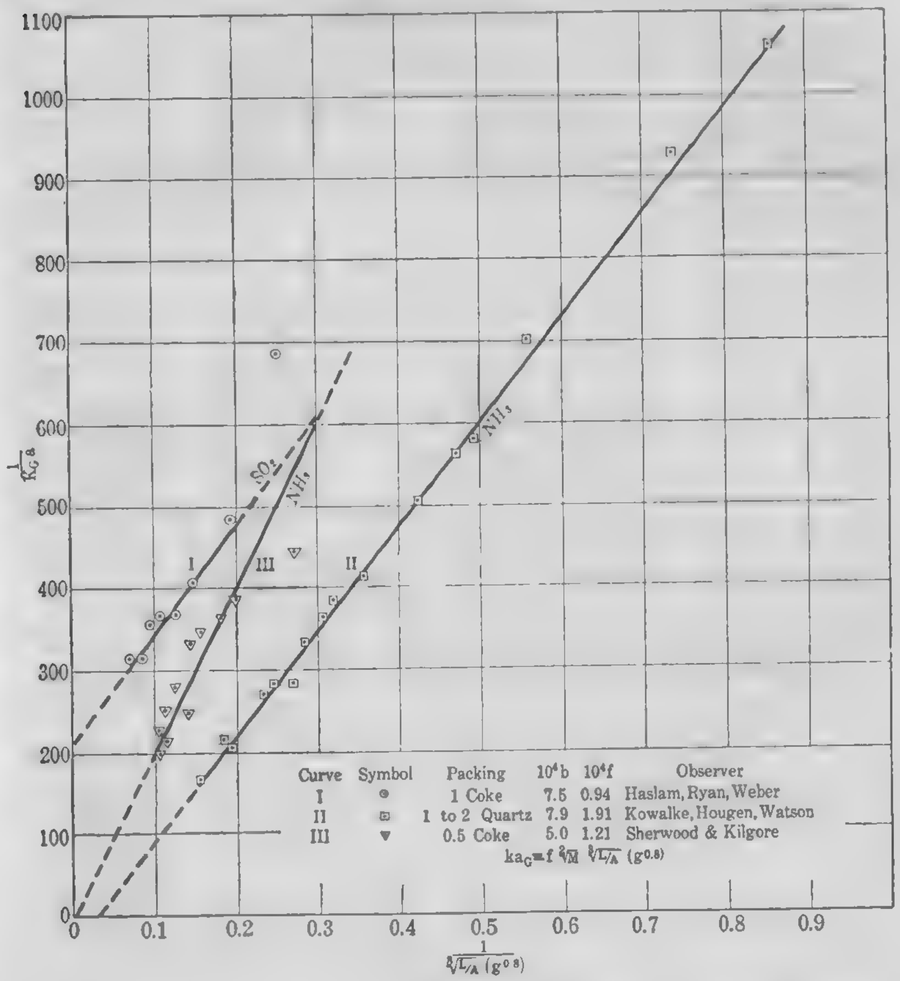


FIG. 191.—Absorption of Gases from Air by Water in Packed Towers.

by water, using towers packed with coke or quartz. The overall resistance $1/K_G a$ are correlated by plotting against $1/\sqrt[3]{(L/A)}(g^{0.8})$, which allows approximately for variations in velocities of gas and liquor. As shown by the intercepts, the liquor-film resistance

[1] HASLAM, RYAN, and WEBER, *loc. cit.*; KOWALKE, HOUGEN, and WATSON, *Chem. Met. Eng.*, **32**, No. 10 (April, 1925), 443; SHERWOOD and KILGORE, *Ind. Eng. Chem.*, **18**, No. 7 (July, 1926), 711.

is negligible for NH_3, as was found to be the case for this gas in a wetted-wall tower. For the absorption of SO_2 from air by water, however, the resistance of the liquor film is a considerable fraction of the total, especially at high velocities of liquid and gas.

Absorption versus Desorption.—The data of Sherwood and Kilgore, shown in Fig. 191, cover both the absorption of NH_3 by water from air, and the removal of NH_3 by air from water. For

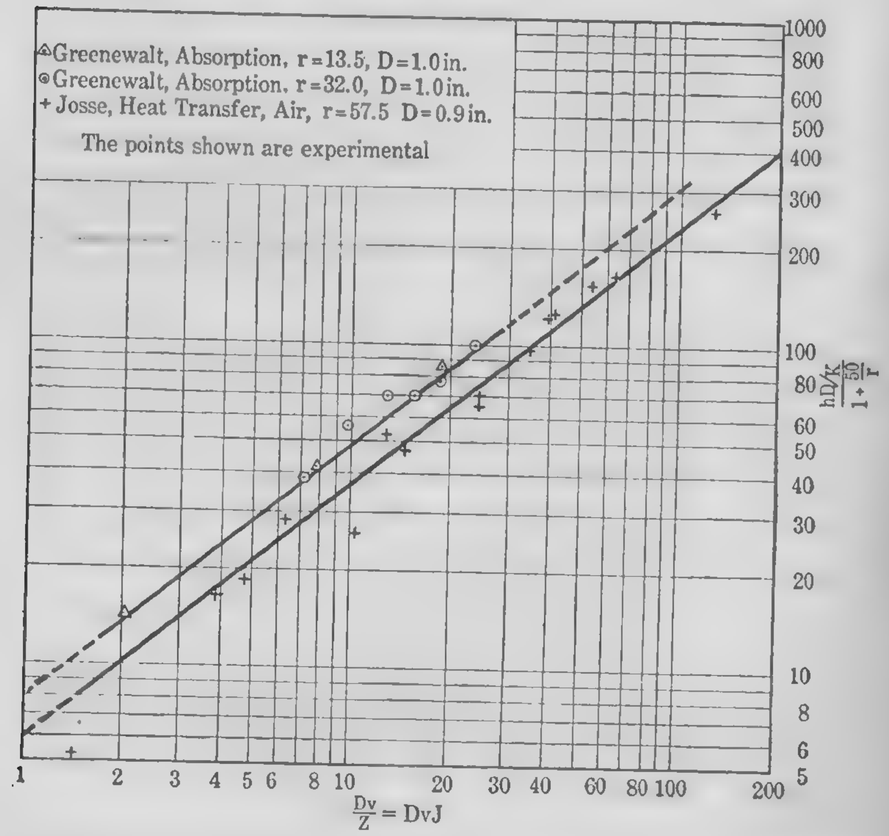


FIG. 192.—Correlation of Data for Heat Transfer in a Pipe and Absorption in a Wetted-Wall Tower.

comparable temperatures and velocities, these data check, regardless of the *direction* of diffusion of NH_3 vapor through the gas film.

Comparison of Absorption and Heat Transfer Process on the Basis of Film Thickness.—According to the film theory, both absorption and heat transfer are controlled by the rate at which the heat or material diffuses through the relatively quiet film of fluid at the boundary (see pp. 36–42). Since for any one fluid the factors controlling film thickness should be the same in

either type of process, for a given diameter, ratio of length to diameter, and gas velocity, one would expect that the film thicknesses would be the same, regardless of whether absorption or heat transfer were taking place. That this is approximately true may be shown by calculating the ratio of diameter to film thickness in similar apparatus, for these two processes.[1]

Greenwalt[2] gives data on the absorption of water vapor from air by sulphuric acid, in wetted-wall towers. His data for two different towers are plotted in Fig. 192. The ordinates show the ratio of diameter to film thickness, corrected for the ratio of length to diameter. The corresponding abscissae show the turbulence factor Dv/z, employing the units of Fig. 37 (p. 141). Figure 192 also shows a plot of the data of Josse[3] for heat transfer to air flowing through a pipe. For equal turbulence, the film thicknesses for absorption are somewhat less than for heat transfer, as should be the case, due to the influence of the water flow in the absorption tower. The correlation is therefore satisfactory and indicates the very striking similarity between absorption and heat transfer.

PART III. DESIGN: GASES BY SOLIDS AND SOLIDS BY LIQUIDS

The adsorption rate of gases and vapors by solid adsorbents is usually rapid. Thus, the air inhaled through the canister of a gas mask is, under extreme conditions, in contact with the adsorbent a total time of only 0.1 or 0.2 sec., and yet in this time the adsorbent will reduce the concentration of mustard gas; for example, to a point below 1 part in 50,000,000 of air. In consequence of this rapidity of adsorption, rate is seldom a controlling factor in determining the capacity of equipment, at least where the adsorbent is in a reasonably fine state of subdivision and possesses high activity. Theoretically, therefore, the amount of solid adsorbent necessary for treating gaseous mixtures is exceedingly small. Thus, for continuous treatment of gas, one could employ two containers, stripping the adsorbed gas from the solid adsorbent in one container while passing the gas through the other. With only a small amount of char in each container, the adsorbing and stripping periods would be very short, requiring too frequent shifting of the gas from one container to another.

[1] W. V. HANKS, private communication.

[2] *Loc. cit.*

[3] *Zeit. des. Ver. deut. Ing.*, **53**, No. 9 (Feb. 27, 1909), 322.

Hence, the amount of adsorbent employed is ordinarily determined by the practical engineering considerations governing the length of this cycle. This also determines the size of the apparatus.

Under normal conditions it is found inadvisable to move solid absorbents, and consequently true continued counter-current operation is not encountered. Where, however, one employs containers of solid adsorbents in systematic rotation (see p. 666), the action is substantially continuous and counter-current, provided the number of absorbers in series at any one time is considerable (5 or above). The effective length of the system, however, is less than the total number of absorbers in operation at any one time. The net length may be assumed to be the total number in actual operation in series, less one half a unit. Otherwise, the computation methods for such a case are identical with those devloped above for continuous counter-current interaction of gases and liquids.

Frequently, however, one employs a small number of absorbent containers, or occasionally gases pass through a single absorber under semi-batch conditions, the gas flowing continuously but the absorber being used until its absorbing capacity is exhausted and then being regenerated or else replaced by a new one.

Illustration 5.—Assume that one has 3,000 cu. ft. per minute of a gas, at 25° C. and normal barometric pressure, containing 1 volume per cent of benzene. It is desired to recover this benzene by adsorption on activated charcoal. Laboratory data show that, at this temperature and concentration, equilibrium will correspond to 0.08 lb. of benzene per pound of carbon. This is somewhat less than the adsorptive capacity of fresh charcoal to allow for the slight decrease in activity which results from continued use. Assume that stripping can be satisfactorily accomplished in 2 hours.

Estimate the minimum number of tanks it is advisable to use and the total tons of char required.

Solution.—Inspection of a characteristic adsorption diagram, such as Fig. 193, shows that in a true counter-current system equilibrium is approached only at the end of the system, whereas in the middle conditions are far removed therefrom. Evidently, therefore, in a stepwise counter-current system the entering gas will saturate successive layers of the absorbent to equilibrium with itself, the cleanup of the gas taking place in the remainder of the system. If now the first unit which the gas enters be not too large a percentage of the whole system, it is entirely practicable to have this unit completely saturated when it is cut out for stripping. Furthermore, because of the extreme rapidity of adsorption in the middle of the system consequent upon the large distance from equilibrium there obtaining, the final unit need not be a small percentage of the total. Normally, $33\frac{1}{3}$ per cent is enough; *i.e.*, if one operates with three units in series, it is possible to saturate the first unit, at least where the adsorption is at all strong, *i.e.*, where the value of n is great. Obviously, it is advisable to cut out a tank each 2 hr., *i.e.*, to operate with four tanks in all.

The amount of benzene removed per hour is calculated as follows:

$$3{,}000\ (60)\left(\frac{273}{298}\right)\left(\frac{0.01}{359}\right)(78) = 359 \text{ lbs.}$$

The char required per tank $= \dfrac{359}{0.08(2000)} = 2.24$ tons. With four tanks one would need a total of 9 tons.

Figure 193 is a modified case of Fig. 174, showing the equilibrium curves OAB for benzene on charcoal and OC for benzene

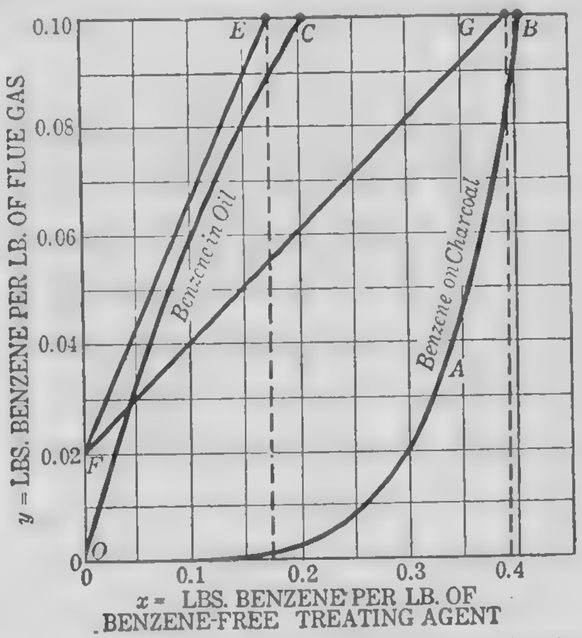


FIG. 193.—Removal of Benzene Vapor from Flue Gas (Problem 5).

in straw oil[1] at 25° C. Since in any absorption operation the operating line must always lie to the left of the equilibrium, mere inspection of this diagram makes it clear that, if one wishes to treat a gas of reasonable benzene concentration, such as represented by y_1, and reduce its concentration to a low figure y_0, not only will it be possible to do this with the use of a much smaller quantity of charcoal than of oil, but in the range of operation where the concentrations are low, it is possible to build

[1] The equilibrium curve for the oil is based on Raoult's law and an average molecular weight of 230 for the oil.

up a far higher driving force with the charcoal than with the oil. In other words, both from the point of view of rate of absorption and carrying power of absorbent, charcoal has the advantage.

Illustration 6.—Referring to Fig. 193, assume that the value of y is 0.10 lb. of benzene per pound of flue gas in the entering gas and 0.02 in the exit gas, corresponding to 80 per cent recovery. Further, assume the operating lines as shown, *FE* for the oil, and *FG* for the charcoal, the fresh treating agent being free of benzene in both cases. Per pound of benzene removed from the gas, this requires only 0.20 lb. of charcoal as compared with 0.47 lb. of oil. Inspection of Fig. 193 makes it obvious that the driving force $y-y_e$ is on the average far higher for the char than for the oil. Moreover, this advantage is greater the lower the concentration of benzene in the initial gas and the more completely it is necessary to strip the gas. It is found that for high concentrations of benzene the many advantages of liquid absorption make the use of straw oil advisable, but for very lean gases the charcoal is superior.

Illustration 7.—A batch of sugar syrup is to be decolorized by finely divided, activated vegetable char, free from color. It is proposed to agitate the char with the syrup at a temperature of approximately 180°. So soon as the syrup is decolorized to 5 per cent of the initial color, the suspension will be sent to a filter for the separation of the decolorized syrup and the spent char. Laboratory data show that at equilibrium between the color to be removed and the char employed in this case the value of n in the Freundlich equation is 3.

Per unit of syrup treated, calculate the ratio of the minimum weight of char required for batch decolorization to the minimum weight of char necessary for ideal counter-current treatment.

Solution.—Figure 194 is a plot of the concentration of color in the syrup y *versus* the color on the char x. The curve *OAE* represents the equilibrium data. For the ideal, single, batch treatment, it is obvious that at the end of the operation the char will be in equilibrium with the syrup; *i.e.*, the abscissa x_2 represents the final color on the char.

The line *FE* in Fig. 194 represents the operating line for the ideal, continuous, counterflow percolation filter. Since the equilibrium curve *OAE* is concave upwards, the best one can do is to obtain equilibrium at the point *E* where the syrup enters, corresponding to the value x_0 on the char. Since in both cases the color is reduced from y_0 to y_2 and the initial char is free from color, a color balance shows that the ratio r of the minimum weights of char in the two cases is equal to x_0/x_2. The values of x_0 and x_2 can be read quantitatively from Fig. 194, or one can use the Freundlich equation: $x_0=a^{1/n}$, and $x_2=ay_2^{1/n}$, whence $r=(y_0/y_2)^{1/n}=20^{\frac{1}{3}}=2.71$. Hence, for this case a single batch treatment would require 2.7 times as much char as continuous counter-current percolation, both processes operating under ideal conditions. It is interesting to note that the ratio of the minimum char requirements of single batch to continuous counter-current percolation depends only upon the ratio of initial to final color, and the value of n in the equation for the adsorption equilibrium, and is independent of the value of the constant a of the Freundlich equation. Furthermore, the smaller the

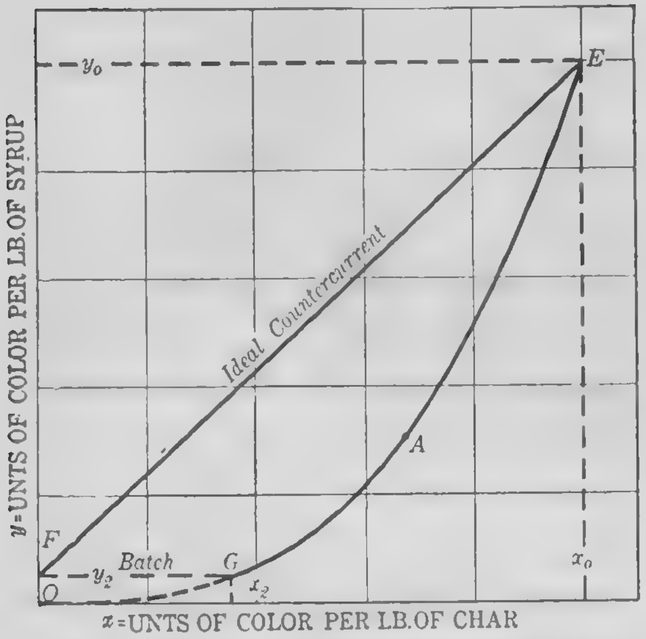


FIG. 194.—Decolorization of Sugar Syrup (Problem 7).

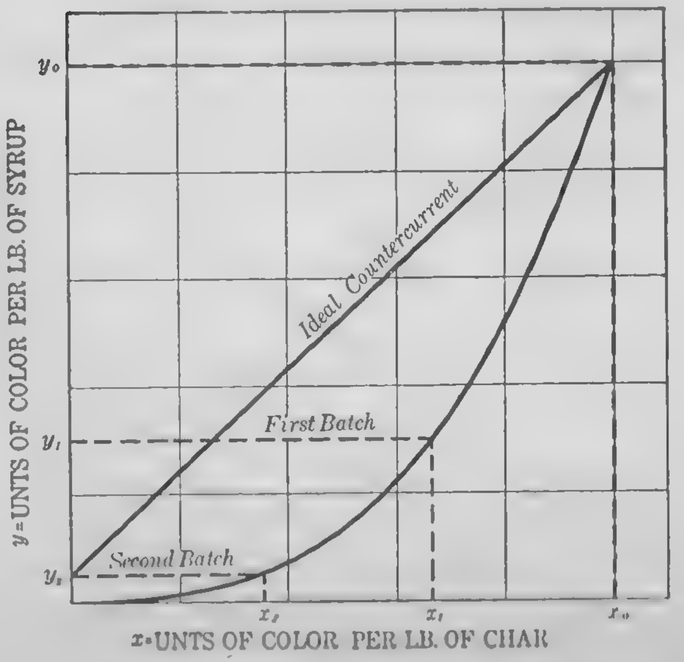


FIG. 195.—Decolorization of Sugar Syrup (Problem 8).

value of n, the greater is the advantage, as regards minimum requirements of char, of continuous counter-flow over a batch treatment.

Illustration 8.—Sugar syrup is to be decolorized by vegetable char as outlined in the preceding illustration, except that two successive batch agitations with color-free char are to be employed instead of one, ultimately reducing the color to 5 per cent of the original value.

Calculate the total minimum char required, expressed as a ratio to the minimum char required in a continuous counter-current decolorization, and report what percentage of the total char should be used in the first of the two batch treatments. Also, compare the total minimum char necessary for two batches with that required for one batch, as computed in the preceding problem.

Solution.—Figure 195 shows a plot of the equilibrium data, with y expressed as units of color per pound of syrup, and x as units of color per pound of char. The color in the syrup is reduced from y_0 to y_1 in the first batch, and from y_1 to y_2 in the second. As specified, $y_2/y_0=0.05$. In the ideal case, at the end of a batch treatment, the color in the liquor would be in equilibrium with the color on the char. Thus, at the end of the first batch, each pound of char would contain x_1 units of color, and after the second batch, x_2. From a color balance, based on 1 lb. of syrup, remembering that the char added in each case is free from color, the total char required W_b would be $\frac{y_0-y_1}{x_1}+\frac{y_1-y_2}{x_2}$.

For the ideal counter-current treatment, since the equilibrium curve OAE is concave upwards, one could have equilibrium at the point C, where the operating line FE intersects the curve. Hence the minimum char for counter-current W_c would equal $(y_0-y_2)/x_0$. Hence the ratio R of the total char for double batches, to the minimum char for continuous counter-current, is given by the following equation:

$$R=\frac{W_b}{W_c}=\frac{\frac{y_0-y_1}{x_1}+\frac{y_1-y_2}{x_2}}{\frac{y_0-y_2}{x_0}} \quad \ldots\ldots\ldots\ldots \quad (a)$$

One can determine the minimum value of the numerator by several methods.

First Method.—If Fig. 195 be drawn to scale, one can arbitrarily select a value of y_1, and by reading the corresponding value of x_1, the total char for the case is determined by the above equation. After assuming various values of y_1, R could be plotted *versus* x_1, and the minimum value of R determined by inspection. From the value of x_1 corresponding to the minimum value of R, a material balance would immediately show what fraction of the total char should be used in the first batch.

Second Method.—If Fig. 195 be not drawn to scale, an algebraic solution can be made as follows. Let z represent that fraction of the initial color y_0 removed in the first batch. The following equations can be written by inspection:

$y_0-y_1=z\ y_0$; $y_1=(a-z)(y_0)$; $y_2=0.05y_0$; $x_0=ay_0^{1/n}$; $x_1=ay_1^{1/n}$; $x_2=ay_2^{1/n}$

By combining these expressions with Eq. (*a*), one obtains

$$R=\frac{1}{0.95}\left[\frac{z}{(1-z)^{1/n}}+(0.95-z)20^{1/n}\right]$$

The minimum value of R may now be found by differentiating R with respect to z and equating to zero, or by assuming various values of z, *i.e.*, by trial and error. One finds that the minimum value of R is 1.81, corresponding to $z=0.7$. Since 70 per cent of the original color is removed in the first batch, $y_1=0.3y_0$, and the proper value of x_1 is determined. From a color balance, one finds that 60.4 per cent of the total char should be used in the first batch.

In order to reduce the color to 5 per cent of the original value, the minimum total char for two successive batch treatments is 1.81 *versus* 2.71 for the single batch, both expressed in terms of the minimum char required for the continuous counter-current decolorization.

Char consumption may be still further reduced by using fresh char only for the second batch and treating the original syrup with spent char from a prior second operation. This may be called stepwise counter-current operation.

APPENDIX I

FLOW OF FLUIDS

1. In a certain chemical plant the lye solution used in the absorption tower is pumped continuously from the bottom of the lye storage tank to the spray head at the top of the absorption tower. The depth of solution in the lye storage tank is constant at 5 ft., and the vertical distance from the bottom of this tank to the spray head is 105 ft. At the prevailing rate of flow, 200 U. S. gal. per min., the friction drop in the pipe and fittings, connecting the storage tank and the spray head, is 15 ft. of lye solution. The static pressure at the spray head is 5 lb. per sq. in. above atmospheric pressure. Both the tower and storage tank are at atmospheric pressure.

Calculate the pump horsepower theoretically required.

Data.—Specific gravity of lye solution is 1.10. The actual inside diameter of the pipe used is 4.03 in.

2. The rate of flow of oil to a number of furnaces fired with a light fuel-oil is being measured with a standard sharp-edged orifice 1 in. in diameter, suitably chambered by a 6-in. steel pipe in the standard manner. The vertical U-tube, employed for the measurement of the differential across the orifice, is completely filled with mercury and oil, and shows a difference in mercury levels of 3 in.

Calculate the flow of oil as U. S. gal. per hr.

Data.—The oil has a specific gravity of 0.900 and a viscosity of 18 centipoises. One cu. ft. equals 7.48 U. S. gallons. The specific gravity of mercury is 13.6.

3. Water at 20° C. is to be pumped from a pond through a 6.07-in. inside diameter galvanized steel pipe line to a point in a plant 10 ft. above the surface of the pond, delivering the water at a rate of 2.0 cu. ft. per sec. and at a pressure of 10 lb. per sq. in. above atmospheric pressure. The line consists of 100 ft. of straight pipe and three standard 90-deg. elbows. Tabulate the numerical values of the various heads involved (expressed as feet of water), and calculate the horsepower theoretically required.

4. Dry air is flowing through a horizontal galvanized iron pipe 4-in. in diameter. In this line is inserted a Thomas flow meter which consists of, first, thermometer No. 1 reading 20.0° C.; second, an electrical heating element, dissipating 1.87 kilowatts; and third, a second thermometer reading 25.0° C. The absolute pressure of the air at thermometer No. 1 is 30.3 in. of mercury while the absolute pressure at thermometer No. 2 is 30.0 in. of mercury.

Calculate the lb. of gas flowing per hr.

5. A petroleum still runs at an average rate of 1,200 bbl. (50 gal. each) per day. The maximum instantaneous running rate may exceed this by

50 per cent. The distillate has a gravity of 0.842. It is desired to insert into the running box an orifice chamber consisting of a vertical chamber with a sharp-mouthed orifice in the middle of the bottom to measure the discharge. The available height of liquid above the orifice plate does not exceed 18 in. The orifice will deliver into a run-off line ample to take away the discharge without any backing up and the feed will be delivered to the side of the orifice chamber at a low velocity so as to introduce no serious turbulence. (*a*) What size orifice should be employed? (*b*) What will be the reading on this orifice if the still is running at 25 per cent of its normal average rate? (*c*) And at its normal rate?

6. California "heavy crude" oil[1] is being pumped at 60° F. through a standard 6-in. steel pipe line at an average velocity of 0.125 ft. per sec.

(*a*) If the average oil temperature be maintained at 120° F., the oil flow remaining unchanged, calculate the percentage reduction in the horsepower required to overcome the friction drop in the line.

(*b*) When the oil is flowing at 60° F., what should be the friction drop as lb. per sq. in. per mile of straight pipe?

7. Illuminating gas at 70° F. is flowing through an 8-in. inside diameter galvanized iron pipe which has been gradually enlarged to 20 in. to form the chambers for a 4-in. orifice drilled in a $\frac{1}{16}$-in. galvanized iron plate, the hole being centered with the center-line of the pipe; 16 in. upstream from the orifice and 8 in. downstream piezometer rings have been installed on the chambers; a vertical U-tube partially filled with water and connected to these piezometer rings, shows a difference in level of 1.21 in. The second U-tube partially filled with water, one arm of which is open to the atmosphere, is attached to the downstream piezometer ring and shows 4 in. of water pressure above atmospheric pressure. The saturated gas has a density of 0.600 referred to saturated air of the same temperature and pressure, the barometer is 29.2 in. of mercury and the vapor pressure of the water at 70° F. is 0.74 in. of mercury. The combined efficiency of fan and motor is 50 per cent and power costs 3 cts. per kw.-hr.

Assuming the gas to be saturated with water vapor, calculate (*a*) the flow as cu. ft. per hr., and (*b*) the power cost of operating the orifice per 24-hr. day.

FLOW OF HEAT

1. An insulated furnace wall consists of $4\frac{1}{2}$ in. of brick *A* followed by 9 in. of brick *B*. The surface temperature of brick *A* on the furnace side is 1,265° F., and the surface temperature of brick *B* on the side exposed to the room is 250° F.

After insulating this furnace with a 2-in. layer of magnesia block (k = 0.040 B.t.u. × ft. per sq. ft. per deg. F. per hr.) the following temperatures were observed.

Surface of brick *A* on the side exposed to the furnace 1,314° F.

Interface, between brick *A* and brick *B*, 1,211° F.

[1] For the sake of illustration, assume that the viscosity data on Fig. 26 (p. 83) apply here.

Interface, between brick *B* and magnesia block, 913° F.

Outer surface of magnesia block, 170° F.

Calculate the heat loss after insulating, expressed as a percentage of the heat loss when bare, neglecting variations of k with temperature.

2. Heat is flowing through a flat slab of insulation, 2 in. thick, on the vertical wall of a Swenson evaporator. The value of k is 0.04 B.t.u. The temperature on the two faces of the insulator are 190 and 90° F.

(*a*) Calculate the B.t.u. flowing per hr. per sq. ft.

(*b*) The cast-iron wall of the evaporator is $\frac{1}{2}$ in. thick, k = 30. Calculate the drop in temperature through the metal.

(*c*) If the value of h from steam to inner wall of the evaporator is 2,000 B.t.u. per hr. per sq. ft. per deg. F., calculate the temp. drop from steam to metal.

(*d*) If the room temperature is 74° F., calculate the value of h from insulation to the room.

(*e*) Calculate the value of H, *i.e.*, the B.t.u. per hr. per sq. ft. per deg. F. from steam to room.

3. In a certain water-tube condenser, h_w = 600 B.t.u. per hr. per sq. ft. of inside surface per deg. F. difference from tube to water. In order to account for this coefficient as due to conduction through a stagnant film of water, assuming k_w = 0.35, how thick would this film have to be, expressed in *inches*?

4. A surface condenser is to operate with steam condensing outside the pipes and cooling water flowing inside the pipes. The copper tube to be used is 1.00 in. inside diameter and has a wall thickness of 0.059 in. Making the assumption given below, calculate the overall coefficient of heat transfer from steam to water based on 1 sq. ft. of outer surface.

Assumptions.—At the water velocity and film temperature involved, the water-side coefficient is 600 per sq. ft. of inner surface. At the steam velocity and temperature involved, the steam-side coefficient is estimated as 2,000 per sq. ft. on the steam side.

5. 10,000 cu. ft. per min. of dry air at 70° F. and normal barometer is to be heated to 170° F. in a tubular heater by means of saturated steam condensing (at constant pressure) at 220° F. around the tubes. The air is to be blown through a number of horizontal 2-in. actual inside diameter cold-drawn steel tubes, arranged in parallel, the tubes being expanded into suitable tube-sheets at the two ends of the apparatus.

Assuming that the initial average air velocity in the tubes is 26 ft. per sec., calculate:

(*a*) Number of pipes in parallel.

(*b*) Length of each pipe.

6. A continuous drier requires 12,800 lb. per hr. of air at a temperature of 170° F. The available air is at a temperature of 70° F. and is to be heated to 170° F. by means of saturated steam condensing at 220° F. inside the vertical pipes of the heater. The air will flow outside and at right angles to the steam pipes. It is proposed to assemble the heater from standard sections already available. Each section consists of one row of parallel vertical pipes, each 3 ft. high, and the section is 17 pipes wide. Each section there-

fore contains 51 lin. ft. of pipe and at the line of pipe centers the clear area for the flow of air between these 17 pipes is 3.55 sq. ft. Since the outside diameter of the steam pipe is 1.281 in., the heating surface per section is 17.1 sq. ft. in contact with the air.

The air flows through a number of such sections in series, each section being staggered with respect to the adjacent sections. For these conditions, Eq. 39 (p. 152) may safely be employed. The specific heat of air is 0.24.

Calculate the number of sections required.

7. Calculate the loss in B.t.u. per 24-hr. day from 100 lin. ft. of standard 1-in. steel pipe carrying saturated steam at 150 lb. gauge pressure through a room at 70° F.,

(*a*) If the pipe be bare.

(*b*) If covered with 2 in. of covering, $k = 0.000165$ gm. cal. (cm.)/(sec.) (sq. cm.) (deg. C.)

Calculate the temperature of the outer surface of the covering.

8. 84.1 lb. per hour of air, at an initial temperature of 70° F., is to be heated while flowing through one 19-ft. length of standard 2-in. steel pipe, heated by means of dry saturated steam condensing in the 3-in. jacket at a constant temperature of 220° F.

Calculate the temperature at which the air will leave the 2-in. pipe.

9. 2,000 U. S. gal. per hr. of a light lubricating oil, at an initial temperature of 200° F., is to be cooled to 90° F., while flowing through a standard 2-in. steel pipe, cooled by the counterflow of water through a jacket of standard 3-in. steel pipe. The water enters at 80° F., and leaves at 100° F.

Calculate the necessary length of the cooler, expressed in feet.

Notes.—For these conditions, the value of H from oil to water is given by the equation: $H = 20u^{0.8}$, where H is expressed as B.t.u. per hr. per deg. F. per sq. ft. of inside surface, and u represents the oil velocity in lin. ft. per sec. The average specific heat of the oil is 0.50, and heat exchange with the surroundings may be neglected. For exact sizes of standard weight steel pipe, see page 101. The oil weighs 7.50 lb. per U. S. gal. and 56.1 lb. per cu. ft.

10. Orrok studied the heat transmission from condensing steam to cooling water in a single-tube surface condenser, obtaining results both for clean and fouled tubes. For each tube the overall coefficient H was determined at a number of different water velocities. The experimental results are well represented by the following empirical equations:

For the old fouled tube: $$\frac{1}{H} = 0.00092 + \frac{1}{268u^{0.8}}$$

For the new clean tube: $$\frac{1}{H} = 0.00040 + \frac{1}{268u^{0.8}}$$

where H is expressed as B.t.u. per hr. per deg. F. overall temperature difference per sq. ft. on the *steam* side, and u = water velocity inside the tube, expressed as ft. per sec.

The tube had inside and outside diameters of 0.902 and 1.00 in. respectively, and was made of Admiralty metal, $k = 63$ B.t.u. (ft.)/(hr.) (sq. ft.) (deg. F.).

From these data calculate the following:

(*a*) Value of $h = k/l$ for the scale or slime deposited in the *old* tube, assuming the *new* tube to be free from deposit, expressing h per sq. ft. on the *water* side.

(*b*) Value of h on the steam side, expressed per sq. ft. on the *steam* side.

(*c*) Film coefficient on water side for a water velocity of 1 ft. per sec., expressed as (B.t.u.)/(hr.) (deg. F.) (sq. ft. on the *water* side).

EVAPORATION

1. A two-effect multiple system of evaporators, with parallel flow of liquor and vapor, is to be designed to concentrate continuously 10,000 lb. per hr. of 10 per cent solution of a colloidal substance to a 40 per cent solution, the temperature of the feed being 170° F. It is planned to use saturated steam condensing at 220° F. in the coils of the first effect and a vacuum over the boiling solution in the second effect such that the solution will boil at 120° F. The condensate from the coils of each effect is withdrawn from the system. Making use of the data and assumptions listed below, calculate the following:

(*a*) Lb. of steam fed per hour.

(*b*) Deg. F. boiling temperature in the first effect.

(*c*) Sq. ft. of heating surface in each effect.

(*d*) Lb. of water evaporated per hour in the first effect.

Notes.—Area of heating surface is the same in each effect and heat losses to surroundings are negligible. Sp. ht. of feed liquor is 0.900. Neglect boiling point raising in each effect and assume overall coefficients of heat transfer in the first and second effects of 300 and 100 B.t.u. per hr. per sq. ft. per deg. F. Assume the latent heats of evaporation are 965 B.t.u. per lb. for the initial steam, 1,000 for that leaving the first effect, and 1,010 for that leaving the last.

2. Plot the data given below as suggested by Duhring's rule and determine the boiling point of the solution at an absolute pressure of 739 mm. of mercury.

The following table shows data for an aqueous solution containing 50.3 per cent by weight of $CaCl_2$.[1]

Boiling temp., deg. C.....	82.10	90.28	95.45	100.85	106.10	110.61
Pressure, mm. mercury.....	112.9	162.4	202.6	253.0	311.6	371.3

3. An aqueous solution of sodium salts of organic acids is to be concentrated in a multiple effect system of evaporators. The liquor is to enter the last effect at 170° F. containing 30 per cent solids by weight and the steam available for the heating surface in the last effect condenses at 165° F. The average production desired is 10,000 gal. per 24-hr. day of liquor containing 40 per cent solids by weight. Using a suitable value of H, calculate the necessary sq. ft. of heating surface in this effect.

[1] BAKER and WAITE, *Met. and Chem. Eng.*, **25**, No. 26 (Dec. 28, 1921).

Per cent Solids	Sp. Gr.	Sp. Ht.	Deg. F., B. P.[1]	Heat of Vaporization (B.t.u./Lb.)	Rel. Fluidity, $1/z$
30	1.32	0.720	110	1,030	0.33
40	1.45	0.615	130	1,019	0.31

[1] Under the vacuum existing in the effect.

Note.—If water were boiling in this evaporator with the same overall temperature difference between steam and boiling liquid, the overall coefficient would be 460 (see p. 395).

4. State the advantage of

(*a*) Film-type evaporators over the submerged-tube type.

(*b*) Submerged-tube evaporators over film type.

5. What are the methods used, both in design and operation of evaporators, to offset evils of

(*a*) Entrainment?

(*b*) Frothing?

6. (*a*) Define boiling point raising and state its disadvantages in evaporation.

(*b*) Name causes of boiling point raising.

HUMIDIFICATION AND DRYING

1. Using vapor pressure data from steam tables, calculate

(*a*) "Humidity" of air saturated at 140° F.

(*b*) "Saturated volume" of air saturated at 140° F., assuming the perfect gas law.

(*c*) Factor necessary to convert (by multiplication) "per cent relative humidity" to "per cent humidity," for air having 50 per cent "relative humidity" at 140° F.

(*d*) The slope of the adiabatic cooling line for initial air having a dew point of 56° F., and a wet-bulb temperature of 100° F.

Tabulate, with the figures just *calculated*, the values read from Fig. 102.

2. Air of 50 per cent humidity at 70° F., is preheated in a hot-blast heater to 170° F. Tabulate the wet-bulb temperature and per cent humidity before and after preheating.

3. The air entering a certain drier has a wet-bulb temperature of 57° F. and a dry bulb of 70° F., and leaves the drier at a temperature of 120° F., with a dew point of 96° F. The wet stock contains 60 per cent moisture and the hourly production is at the rate of 1,500 lb., averaging 15 per cent moisture. Using the humidity chart, calculate:

(*a*) Cu. ft. per min. of entering air, its dew point and per cent humidity.

(*b*) B.t.u. per hr. supplied by heating surface within the drier, neglecting the heat capacity of the bone dry stock, and

(*c*) Wet-bulb temperature and per cent humidity of exit air.

4. A drier is to be designed to reduce the water content of a certain material from 180 to 10 per cent (dry basis). In order to produce the desired drying conditions, the entering air is to have a temperature of 120° F. and a humidity of 0.0110 lb. of water per lb. of dry air, and the exit air will leave at 110° F. with 70 per cent humidity. On the basis of 1,000 lb. of product per hour, and neglecting the heat capacity of the bone-dry stock, calculate:

(*a*) Air entering the drier as cubic feet per minute.

(*b*) B.t.u. per hr. to be supplied by the heating surface within the drier.

(*c*) B.t.u. per hr. to be supplied by the preheater, if the air enters same at 70° F.

(*d*) Total B.t.u. consumed per lb. of evaporation.

(*e*) Air entering preheater at 70° F., as cu. ft. per min.

(*f*) Tabulate temperature of the "dry bulb," "wet bulb," and "dew point" for the air entering the preheater, the air entering the drier, and the air leaving the drier.

5. Flue gas containing methanol vapor is flowing at high velocity through a 4-in. pipe. The dry-bulb temperature is 199° F., and the total absolute pressure is 760 mm. of mercury. The wick covering on the bulb of a second thermometer is kept properly wetted with liquid methanol, and the reading of this thermometer is 68° F. The flue gas contains a negligible amount of water vapor.

Referring to the data and notes given below, calculate.

(*a*) Actual humidity of the gas, expressed as lb. of methanol vapor per lb. of flue gas.

(*b*) Initial condensing temperature or dew point of the gas.

(*c*) Per cent methanol vapor in the gas.

Data.—Specific heats, expressed as B.t.u. per lb. per deg. F., are 0.42 for the flue gas itself, and 0.35 for the methanol vapor. Latent heat of vaporization of methanol, at 68° F., is 504 B.t.u. per lb. The molecular weights are 32 for methanol and 31.2 for the flue gas.

VAPOR PRESSURES OF METHANOL

Temp., deg. F.	32	50	68	86	104	122	199
Mm. of mercury	29.6	54.7	96.0	160	261	406	3,350

6. A cooling tower 2,200 cu. ft. in volume, gave on test the following data:

Temperature of water entering the top = 105° F.

Temperature of water leaving the bottom = 84.7° F.

Temperature of air entering the bottom = 71° F.

Temperature of air leaving the top = 90° F.

Humidity of the air entering the bottom = 0.0062.

Humidity of the air leaving the top = 0.0295.

Volume of air entering the tower = 55,900 cu. ft. per min.

Volume of water cooled = 651 gal. per min.

If the temperature of the entering air were to rise to 100° F. with its absolute humidity remaining unchanged, which might happen between morning and noon of a summer day, the weight of air and water remaining the same as before, to what temperature would the water be cooled?

7. Wood chips are to be dried in a continuous counterflow rotary drier solely at the expense of the heat of the air flowing through the drier. It is estimated that heat losses from the outer surface of the drier will be negligible. The chips enter with 40 per cent moisture (wet basis) and leave with 15 per cent moisture (wet basis), and the drier is to deliver 2,000 lb. of product per hr. The air enters the drier at 230° F. with a humidity of 0.010 and leaves at 120° F. As a result of suitable small-scale experiments it has been determined that the actual air velocity must at no point exceed 8 ft. per sec., as otherwise chips may be blown from the drier. The chips must remain in the drier 2 hr. in order to provide adequate time for the diffusion of the moisture from the interior of the chips to the surface. The average size of the chips is 1 by 2 by ¼ in. thick, and the chips occupy 0.17 cu. ft. per lb. of bone dry chips. The barometer may be assumed to be normal.

What should be the length and inside diameter of the drier in ft. if the ratio of length to diameter be taken as 5 to 1?

8. From a consideration of the drying data given below, what conclusion may be drawn regarding the rate of drying of this particular sample?

DATA

(1)	245	212	192	155	129	107	85	82
(2)	0	105	170	305	380	454	523	548

(1) Per cent total water based on bone-dry weight.

(2) Time in minutes.

9. The production of a certain drier is 1 ton per hr., and the percentage of moisture on the wet basis is reduced from 50 to 15 per cent. The humidity of the air passing through the drier rises from 0.0100 to 0.0200, while the air temperature falls from 155 to 100° F. Assuming 1,055 B.t.u. consumed per lb. of evaporaton, calculate the ratio of the heat lost to the surroundings to that removed from the air in the drier.

DISTILLATION

1. For mixtures of benzene and toluene, construct the following plots, all on one sheet. Assume that the laws of Raoult and Dalton apply.

(*a*) Equilibrium diagram for constant pressure of one atmosphere, plotted with y, mol fraction of benzene in the vapor, as ordinates *versus* x, mol fraction of benzene in the liquid, as abscissae.

(*b*) The boiling point as ordinates *versus* x.

(*c*) Relative volatility, α, *versus* x.

(*d*) Curve of y *versus* x computed from the equation on page 591, and the average value of α.

DATA

Vapor pressures of benzene and toluene given below are taken from Landolt-Bornstein Tabellen (1912)

Benzene		Toluene	
Deg. Cent.	P_B Mm. of Mercury	Deg. Cent.	P_T Mm. of Mercury
70	547	110.4	760
80	754	105.3	650
90	1016	99.4	550
100	1344	93.2	450
110	1748	85.5	350
		80.9	300

(*e*) Plot weight fraction of benzene in the *vapor*, C, as ordinates *versus* the weight fraction of benzene in the *liquid*, c, assuming molecular weight of each component is same in both liquid and vapor.

2. For a simple distillation at constant temperature, show that, if Raoult's Law apply,

$$\frac{-dA}{-dB} = \alpha \frac{A}{B},$$

where A is the mols of the more volatile component left in the liquid in the still at any time, and B is the mols of the less volatile remaining in the liquid at this time. Show that this equation is a special form of the Rayleigh equation (p. 598). Integrate the equation. Show that it applies to any two components of a multicomponent mixture, if these two follow Raoult's Law, or if they deviate from it equally in direction and degree.

3. A solution containing 60-weight per cent benzene and 40-weight per cent toluene is subjected to a simple batch distillation at atmospheric pressure. For the purpose of this problem assume $\alpha = 2.55$.

(*a*) If the distillation be discontinued when the weight of the distillate amounts to 50 per cent of the weight of the charge, calculate:

1. The concentration of the mixed distillate, as weight per cent benzene.

2. The concentration of the liquid left in the still, as weight per cent benzene.

3. The amount of benzene in the distillate, expressed as a percentage of the amount of benzene in the charge.

(*b*) If the distillation be discontinued when 90 per cent of the original benzene is in the distillate, calculate

1. The concentration of the mixed distillate, as weight per cent benzene.

2. The concentration of the liquid left in the still, as weight per cent benzene.

3. The weight of the distillate, expressed as a percentage of the weight of the charge.

4. A mixture of 50 g. of benzene and 50 g. of toluene is subjected to a simple batch distillation, at atmospheric pressure. Plot boiling points as ordinates versus weight per cent of the charge distilled off as abscissae.

Notes.—Raoult's law applies. The vapor pressures of the individual components are given in Problem No. 1.

5. A certain plant is discarding 50,000 lb. per 24 hr. of an aqueous solution saturated with aniline at 20° C. In order to recover aniline, it is proposed to subject this solution to a batch distillation at atmospheric pressure, allowing the vapors to pass directly to a condenser and cooler from which distillate at 20° C. is collected as fast as formed. This cold distillate is immediately separated into two layers, the aniline layer being collected as product and the water layer being reserved for the next batch distillation. The bottoms left in the still at the end of the run are discarded.

Using the assumptions and data given below, calculate:

(*a*) When 80 per cent of the aniline of the charge has been distilled off, what per cent of the water in the charge will have been vaporized?

(*b*) Under these conditions, per lb. of aniline in the aniline layer of the distillate, how many B.t.u. are supplied as latent heat in the steam fed to the coils?

Notes.—The still and the vapor main are sufficiently insulated so that the effect of heat losses to the surroundings is negligible. Assume that the temperature of the liquid in the still remains substantially constant at 99° C. At 99° C. the vapor pressure of pure aniline is 44.0 mm. of mercury and the vapor pressure of pure water is 733 mm. of mercury. At 99° C., aniline saturated with water contains 31.6 mol-per cent of water, and water saturated with aniline contains 1.42 mol-per cent of aniline. At 20° C. water saturated with aniline contains 0.615 mol-per cent of aniline, and aniline saturated with water contains 21.4 mol-per cent of water. Molecular weights of aniline and of water are 93.1 and 18.0 respectively. At 99° C., latent heats of vaporization of water and aniline are 971 and 240 B.t.u. per lb. respectively. Sp. gr. of aniline is 1.024 at 20° C.

6. A mixture of benzene and toluene is fed, slowly and continuously, into the upper end of a slightly inclined tube, where liquid and vapor in equilibrium with it flow gradually in parallel streams to the lower end of the tube. Bottoms and vapors are separated and withdrawn at this end of of the tube. The inclined tube is being heated from the outside and while the temperature of the contents may vary from point to point near the entrance, the mixture is at constant temperature in the latter portion. The feed contains 50 per cent benzene by weight. The total pressure is normal barometric and Raoult's law applies.

Calculate and plot boiling point at the exit, versus weight per cent of charge distilled over.

7. It is desired to design a bubble-plate column for the continuous separation of benzene and toluene at atmospheric pressure. The feed contains 70 mol-per cent of benzene, and enters the column properly preheated. The distillate is to contain 99 mol-per cent of benzene and the bottoms are to contain 99 mol-per cent of toluene. Other data are given below.

(*a*) If an infinite number of plates were available, calculate the theoretically minimum ratio of reflux to vapor in the enriching section.

(*b*) In designing the actual column it is proposed that the molal ratio of reflux to vapor, in the enriching section, be 0.667. For these conditions, calculate:

1. Total number of theoretically perfect plates required.

2. Location of the feed plate, calling the top plate in the column number 1. What will be the composition of liquid on the feed plate?

Data and Notes.—The entire column is directly connected to a still heated by saturated steam condensing at 100 lb. gauge pressure inside a heating coil. The vapors from the top of the column enter a simple, total condenser, part of the condensate being returned hot to the top plate, as reflux, the remainder being cooled and withdrawn as distillate. The molal overflow may be assumed constant, except as affected by the introduction of the feed. The equilibrium relation between liquid and vapor composition, calculated from Raoult's law, is given in the subjoined table, compositions being expressed as mol fractions of benzene.

x	0	0.113	0.258	0.407	0.580	0.776	1.00
y	0	0.262	0.456	0.628	0.776	0.898	1.00
B.P., deg. C.	110.4	105	100	95	90	85	80.3

3. If the still is to handle feed at the rate of 12,000 lb. per hr., and the maximum allowable vapor velocity is 2 cu. ft. per sec. per sq. ft. of total cross-section, what must be the inside diameter of the column? How many lb. per hr. of steam are required by the heating coil?

Note.—Latent heat of condensation of dry, saturated steam, at 100 lb. gauge, is 880 B.t.u. per lb.

8.[1] An experimental packed column is being operated at atmospheric pressure to strip ammonia from an ammonia liquor, the heating being accomplished solely at the expense of dry, saturated atmospheric steam fed in at the base of the column. A test on this column gives the data tabulated below.

RESULTS WITH PRESENT COLUMN

	Lb. Per Hr.	Per Cent NH_3 by Wt.
Feed	10.0	1.50
Product	1.33	9.50
Waste	11.47	0.20
Steam	2.80	

It is desired to increase the height of the present column in order to be able to strip the waste to a concentration of 0.03 per cent NH_3 by weight. If in the enlarged column the steam fed at the bottom is twice the theoreti-

[1] For additional problems on steam distillation, see pp. 737–738.

cally minimum amount, calculate the height of the enlarged column expressed as a percentage of the present height.

Notes.—In all cases the feed is at 70° F. For the present it is agreed to assume that the individual coefficients k_G and k_L are equal (see p. 689). The equation of the equilibrium diagram, for the concentrations involved, is $y = 12.6x$, where y = *weight* fraction of ammonia in the vapor and x = *weight* fraction of ammonia in the liquor. $(k_G a)(A)(dL)(y_e - y) = (k_L a)(A)(dL)(x - x_e)$ = Lbs. NH_3 removed per hour.

9. A solution of ethanol in water, containing 8 per cent ethanol by weight, is to be stripped in a continuous exhausting column operated at atmospheric pressure. The feed, at the boiling point, enters on the top plate and flows down the column, while saturated steam is blown in below the bottom plate. The product of the column is the vapor from the top plate, and there is no reflux or overflow other than the feed itself. The product is to contain 99 per cent of the alcohol in the feed.

(*a*) For a column containing an infinite number of plates, calculate the *minimum* mols of steam required per mol of feed, the corresponding maximum mol per cent of alcohol in the product, and the mol per cent alcohol in the liquid on the feed plate.

(*b*) Assume that in the actual column, the mols of steam injected per mol of feed are twice the minimum calculated above. For these conditions, compute the number of theoretically perfect plates required, the mol-per cent of alcohol in the product, and the mol-per cent of alcohol in the liquor on the top or feed plate.

Notes.—To simplify calculations, assume equal molal latent heats of vaporization of both water and alcohol, neglect the effect of temperature gradient throughout the column, assume heat losses are negligible, and that there is no heat effect of mixing liquid with liquid, or vapor with vapor. Neglect the effects upon both boiling points and vapor compositions, of the pressure gradient through the column.

The following table (taken from Fig. 145, p. 590) gives the equilibrium values of *C versus c* expressed in weight fractions of alcohol in vapor and liquid, respectively.

c.	0.02	0.04	0.060	0.08	0.10
C	0.155	0.32	0.465	0.538	0.58

10. The following problem deals with derivations and proofs regarding continuous rectification of a mixture of two liquids which are mutually miscible in all proportions. Make the usual simplifying assumptions leading to the constancy of molal overflow except as affected by the introduction of the feed itself. The feed enters the bubble-plate column properly preheated. The vapors leaving the top of the column enter a total condenser, part of the hot condensate being returned as reflux to the top plate, the remainder being drawn off as product through a liquid cooler. The column is attached to a suitable still heated by steam condensing inside closed coils. No live steam is blown into the column. The equilibrium curve is of the normal type, having no constant boiling-point except where $x = 0$ and $x = 1$.

(*a*) Derive the equation of the enriching line.

(*b*) Derive the equation of the stripping line.

(*c*) Prove that these two operating lines intersect at $x = x_f$.

(*d*) Prove that the enriching line intersects the diagonal $(y = x)$ at $x = x_e$.

(*e*) Prove that the stripping line intersects the diagonal $(y = x)$ at $x = x_w$.

(*f*) Prove that the minimum ratio of reflux to vapor in the enriching section, O_{n+1}/V_n equals $(x_e - y_f)/(x_e - x_f)$.

(*g*) When using this minimum ratio of reflux to vapor explain why an infinite number of plates is required.

(*h*) When, in the enriching section, the ratio of reflux to vapor is unity show that the operating line coincides with the diagonal $y = x$.

11. (Oxygen Column). Liquid air is fed to the top of a bubble-plate stripping column operated at substantially atmospheric pressure. Sixty per cent of the oxygen in the feed is to be drawn off in the vapor from the still, and this vapor is to contain 0.2 mol per cent of nitrogen. Based on the assumption and data given below, calculate:

(*a*) The purity of the crude nitrogen vapor leaving the top plate, expressed as mol per cent of nitrogen.

(*b*) The mols of vapor generated in the still per 100 mols of feed.

(*c*) The number of theoretically perfect plates required.

Notes.—To simplify the problem, assume that the molal overflow is constant throughout the column, and is equal to the mols of feed. Liquid air contains 21 mol-per cent of oxygen and 79 mol-per cent of nitrogen. The equilibrium data of Baly[1] are shown below.

Temperature, Deg. Kelvin	Mol Per Cent N_2 in Liquid	Mol Per Cent N_2 in Vapor
77.5	100.0	100.0
78.0	91.9	97.8
80.0	66.8	88.0
82.0	47.8	76.4
84.0	33.8	63.1
86.0	22.2	47.8
88.0	12.4	30.4
90.0	3.8	10.2
91.0	0.0	0.0

12. (Nitrogen Column). Liquid air is fed at an intermediate point between the top and bottom plate of a bubble-plate column operated at sub-

[1] *Phil. Mag.* **5**, No. 49, June 1900, p. 517.

stantially atmospheric pressure. The crude nitrogen vapor leaving the top of the enriching section is to contain 99.8 mol-per cent of nitrogen. In this case no vapor is drawn off from the still, but liquid is drawn off from the still attached to the bottom of the enriching section. This liquid is evaporated in the jacket of a reflux condenser just above the top of the enriching section.

With an infinite number of perfect plates available, what would be the maximum purity of liquid drawn off from the still? Under these conditions, what is the corresponding percentage recovery of nitrogen?

ABSORPTION AND EXTRACTION

1. Water contains organic color which is to be extracted with alum and lime. Five parts of alum and lime per million parts of water will reduce the color to 25 per cent of the original color, and 10 parts will reduce the color to 3.5 per cent.

Estimate how much alum and lime as parts per million are required to reduce the color to 0.5 per cent of the original color.

2. Fifty parts of copperas and lime per million parts of dye-house effluent removes 50 per cent of the color. How much will be required to reduce the color to 10 per cent, if $n=8.5$?

3. Cotton is piled loosely in a steel chamber which is gradually evacuated to 20 mm. of mercury absolute pressure. The cotton charged at 24° C. contains 4.77 per cent of moisture (wet basis) and as piled contains 0.8 lb. of water-free cotton per cu. ft. The barometer is 760 mm., the sp. gr. of the dry cotton is 1.48, and the heat capacity of the cotton is sufficient to prevent appreciable change in temperature during evacuation.

Calculate the *ultimate* moisture content of the cotton (wet basis) after evacuation.

Data.—At 24° C. cotton containing 5.00 per cent of moisture (dry basis) is in equilibrium with air containing 8.3 mm. of water vapor, and cotton containing 2.00 per cent of water (dry basis) is in equilibrium with air containing 1.65 mm. of water vapor.

4. In the impregnation of cord-tire fabrics with rubber the fabric is passed through a bath of rubber cement. The benzene (C_6H_6) is evaporated from the fabric into flue gas which flows through the drier in a direction opposite to the travel of the fabric, the heat being supplied by steam coils within the drier. The flue gas leaves the drier at 140° F. containing 40 per cent of benzene vapor by volume, and is cooled to 70° F. in a cooler of the surface-condenser type. The evaporation of solvent in the drier amounts to 200 U. S. gal. of benzene per hr., and the barometer is 30.0 in. of mercury. Average Orsat analysis of the gas is 15 per cent CO_2, no CO, and 5.9 per cent O_2. Sp. gr. of benzene is 0.880.

Calculate:

(*a*) Per cent recovery in the cooler.

(*b*) Temperature at which condensation begins in the cooler, and

(*c*) Cost of coke as cts. per gal. of benzene recovered in the cooler, assuming no flue gas recirculated and coke containing 85 per cent carbon to cost $8 per short ton.

5. The gases leaving the fore-cooler of Problem No. 4 are compressed in two stages to a final pressure of 132.3 lb. gauge. At the end of the first stage the gas is cooled to 70° F. in the inter-cooler. The gas leaving the intercooler is compressed to the final pressure and then cooled to 70° F. in an after-cooler. Assume the ratio of the effective cylinder displacements in the two stages to be the standard one, *i.e.*, such that the absolute pressure in the intercooler is the geometric mean of the absolute pressures entering the first stage and leaving the last stage.

Calculate:

(*a*) Per cent recoveries in inter-cooler and after-cooler.

(*b*) Temperature of gases entering the after-cooler and the horsepower theoretically required in the second stage of the compression (see p. 97).

The value of k, or (c_p/c_v), equals 1.404 for O_2, 1.404 for N_2, 1.30 for CO_2, and 1.10 for benzene.

6. A plant using benzene as a rubber solvent evaporates this solvent into flue gas and recovers the benzene therefrom by absorption in a very high-boiling mineral oil. Over the range of concentrations involved, Raoult's Law applies when the average molecular weight of the oil is taken as 220. The solution of benzene in the oil is denuded of benzene by vacuum steam distillation at a temperature of 300° F., employing steam superheated to 300° F. The operation is carried out in a countercurrent tower supplied with the necessary heating surface properly distributed to maintain substantially constant temperature throughout the tower. The rich oil enters this tower containing 3 per cent of benzene by weight and is preheated to 300° F.

At 300° F., the pressure of pure benzene is 4,400 mm. The condensing temperature is 90° F., at which temperature the vapor pressure of benzene is 138 mm. and that of water 36.0.

(*a*) For complete stripping of the oil, what is the theoretically minimum amount of steam per lb. of benzene recovered by the distillation, assuming a tower of sufficient height so that substantial equilibrium between steam and oil could be secured?

(*b*) Now assume that a tower of sufficient height be operated with the theoretically minimum amount of steam. What would be the minimum weight per cent of benzene in the oil leaving the bottom? To what per cent removal of the original benzene does this correspond? What is the corresponding minimum consumption of injected steam?

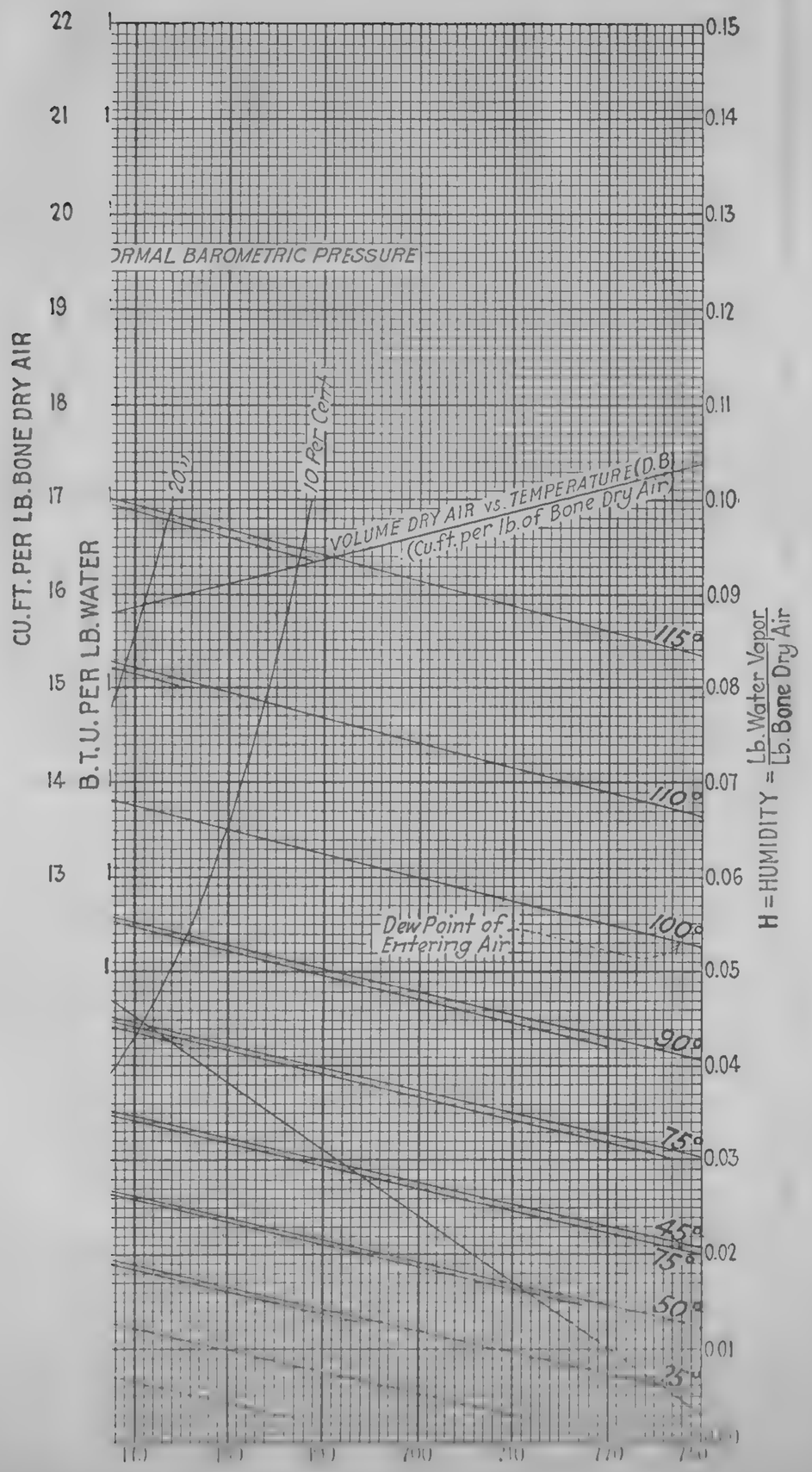
(*c*) Now assume that enough steam is fed so that the molal ratio of benzene to steam in the vapors to condensers equal 2.8, and that the column is sufficiently tall so that equilibrium could be obtained. To what per cent removal of the original benzene does this correspond? Calculate the lb. of injected steam per lb. of benzene removed as distillate.

(*d*) If colder condenser water be available so that the effective condensing temperature can be reduced to 70° F., at which temperature the vapor pressure of benzene is 67 mm., and that of water 18.8, by what per cent could one expect to reduce the steam consumption per lb. of benzene as compared with part (*a*), operating under conditions to give substantially complete stripping?

7. A tower is being designed for the continuous stripping of benzene from a non-volatile oil by means of superheated steam, employing a packed column operated under vacuum, the total pressure being 200 mm. of mercury. The operating temperature is held constant at 300° F. by means of high-pressure steam condensing inside closed coils properly distributed throughout the column. The feed contains 1.5 per cent benzene by weight and is preheated to 300° F.

In making a preliminary design it is agreed that the steam is to remove 90 per cent of the benzene present in the feed and that the minimum driving force, $y_e - y$, is to be taken as 0.05 mols benzene per mol of steam. For this condition, calculate the lb. of superheated steam injected per lb. of benzene distillate.

Notes.—The gas film resistance to diffusion may be taken as of controlling importance. At 300° F., the vapor pressure of pure benzene is 4,400 mm. of mercury. The molecular weights of steam, benzene, and benzene-free oil are 18, 78, and 220, respectively. Raoult's Law applies at equilibrium.



HUMID HEAT (B.t.u. per deg. fahr. per lb. Bone Dry Air)

0.24 0.25 0.26 0.27 0.28 0.29 0.30 0.31

LATENT HEAT OF STEAM (B.t.u. per lb. H_2O) vs. TEMPERATURE

HEAT (B.t.u. per deg. fahr. per lb. Bone Dry Air) vs. HUMIDITY

HUMIDITY vs. TEMPERATURE

SATURATED VOLUME vs. TEMPERATURE (O.B.)
(Cu. ft. per lb. Bone Dry Air)

BASIS = NORMAL BAROMETRIC PRESSURE

100 Per Cent

90 "

80 "

70 "

60 "

50 "

40 "

30 "

20 "

10 Per Cent

VOLUME DRY AIR vs. TEMPERATURE (O.B.)
(Cu. ft. per lb. of Bone Dry Air)

115°

110°

100°

90°

75°

45°

75°

50°

25°

Dew Point of Entering Air

1100 1090 1080 1070 1060 1050 1040 1030 1020 1010 1000 990 980 970 960 950

0.15 0.14 0.13 0.12 0.11 0.10 0.09 0.08 0.07 0.06 0.05 0.04 0.03 0.02 0.01 0.00

H = HUMIDITY = Lb. Water Vapor / Lb. Bone Dry Air

50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230

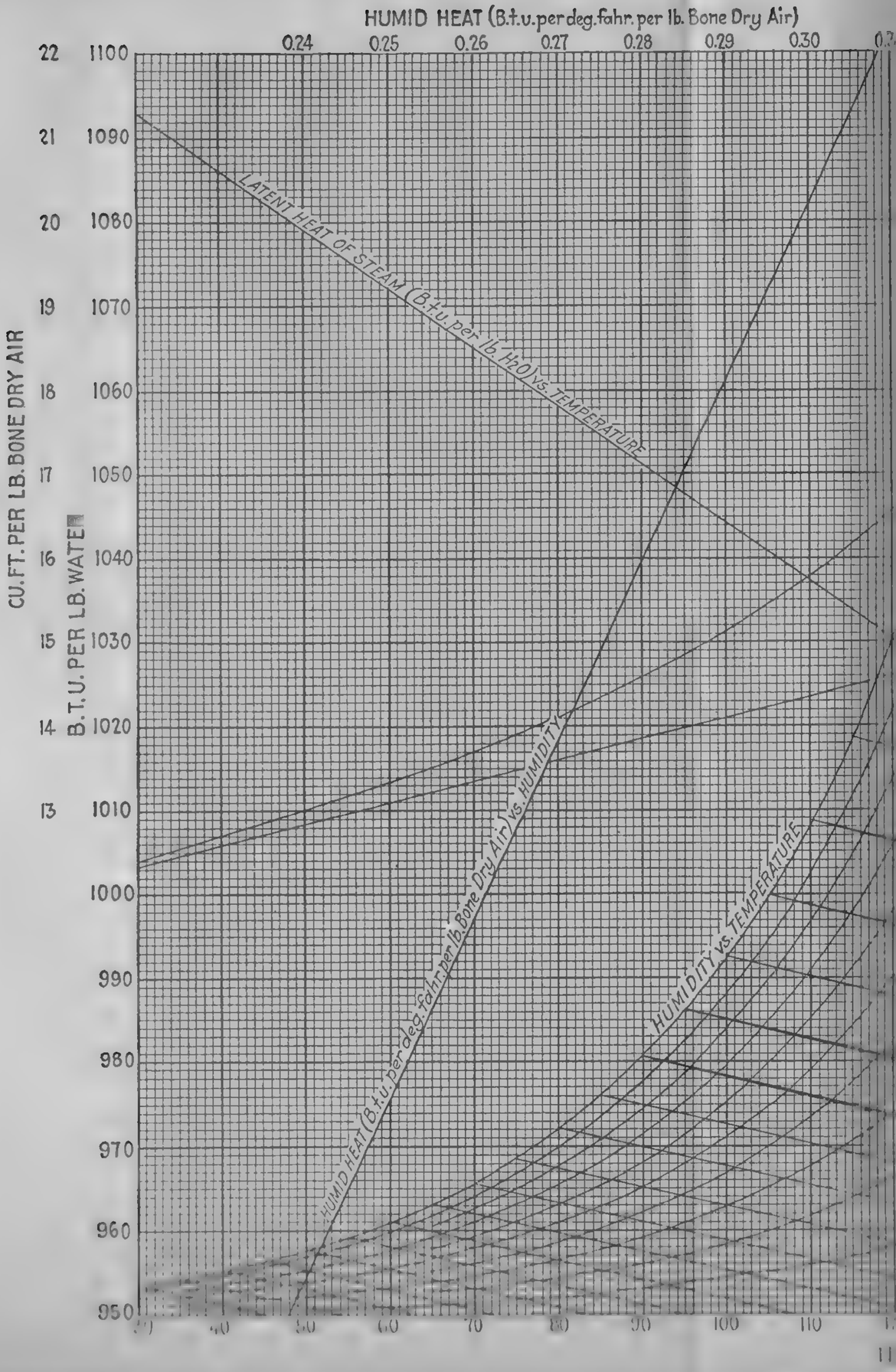
TEMPERATURE, DEG. FAHR.

(Facing page 738)

7. A tower is being designed for the continuous stripping of benzene from a non-volatile oil by means of superheated steam, employing a packed column operated under vacuum, the total pressure being 200 mm. of mercury. The operating temperature is held constant at 300° F. by means of high-pressure steam condensing inside closed coils properly distributed throughout the column. The feed contains 1.5 per cent benzene by weight and is preheated to 300° F.

In making a preliminary design it is agreed that the steam is to remove 90 per cent of the benzene present in the feed and that the minimum driving force, $y_e - y$, is to be taken as 0.05 mols benzene per mol of steam. For this condition, calculate the lb. of superheated steam injected per lb. of benzene distillate.

Notes.—The gas film resistance to diffusion may be taken as of controlling importance. At 300° F., the vapor pressure of pure benzene is 4,400 mm. of mercury. The molecular weights of steam, benzene, and benzene-free oil are 18, 78, and 220, respectively. Raoult's Law applies at equilibrium.



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